

URBAN PRECURSORS AND THEIR PHOTOCHEMICAL PRODUCTS

T. E. Graedel
Bell Laboratories
Murray Hill, New Jersey

SUMMARY

Many aspects of the photochemical processes in the troposphere near and within urban areas have recently been explored by kinetic computer modeling. Comparison with the results of data analyses indicates that features of and patterns in air quality data can be semiquantitatively reproduced for a variety of geographical and chemical situations. Results are presented for calculations representing urban workdays, urban Sundays, transport and chemistry upwind of, within, and downwind of urban areas, and overwater transport. The effects of incomplete or insufficiently accurate information on the results of photochemical calculations are described. A current limitation in the detailed validation of these theoretical chemical studies is a sparseness of data on reactive free radicals, on inorganic photochemical products, on organic reactants and products, and on certain of the applicable meteorological processes. Appropriate chemical and meteorological measurements needed to alleviate these interpretive limitations on the understanding of urban tropospheric processes are discussed.

INTRODUCTION

An initial determination of air quality in urban atmospheres is provided by measurements of emitted trace species known to be undesirable: carbon monoxide, sulfur dioxide, benzene, and so forth. A more detailed assessment includes evaluations of the presence and concentrations of the chemical products of these precursors. Although the product compounds are crucial constituents of many atmospheric processes, little information is presently available concerning their concentrations, reactions, or lifetimes in ambient air.

A variety of approaches promises to ameliorate this situation. Laboratory studies of individual reactions provide vital information on reaction rates and products. Another technique that has been useful over the years has been the monitoring of products in smog chamber experiments. More recently, improvements in computer codes for kinetic simulations of large chemical systems have resulted in the development of models of the chemistry of the urban atmosphere. The results produced by all these techniques, together with confirmatory field measurements, are necessary for an improved chemical understanding of the atmosphere. Of particular interest from a chemical standpoint are the interrelationships between the precursors and their atmospheric products.

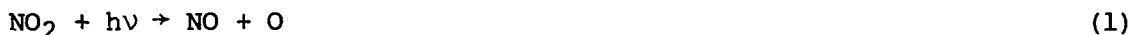
This paper¹ attempts to define the most significant of the precursor-product combinations in the urban atmosphere, together with the chemical intermediates that link them. A survey of recent results of kinetic computer modeling of the northern New Jersey atmosphere is then presented, and the accomplishments and limitations of such approaches are discussed. Finally, suggestions for field measurements of particular interest to the atmospheric chemist are made.

The discussion herein is restricted to the gas phase, despite substantial evidence that certain effects, particularly the removal of oxygenated photochemical products, may be controlled by gas-surface interactions and subsequent aerosol chemistry. Among the important processes are the formation of sulfate and nitrate aerosols, the loss of ammonia to form ammonium salts in aerosols, and the oxidation of alcohols, aldehydes, and ketones to carboxylic acids on aerosol surfaces. A recent review of these topics has been given by the Subcommittee on Ozone and Other Photochemical Oxidants (ref. 1). Further information and the incorporation of aerosol chemistry into kinetic models will doubtless be topics of active research interest within the coming years.

CHEMICAL REACTION CHAINS IN URBAN ATMOSPHERES

The chemical processes in urban atmospheres utilize anthropogenically emitted compounds as precursors for the formation of a variety of more highly oxygenated products. Solar radiation is an important constituent in these chemical reaction chains, since photodissociation of several common emittants produces the reactive free radicals that control most of the chemistry.

A simple schematic overview of a central reaction chain in urban atmospheres is shown in figure 1. The chain utilizes the aldehyde (RCHO), nitric oxide (NO), and hydrocarbon (HC) species that are common anthropogenic emittants to produce large numbers of free radicals and oxygenated products. The complete cycle shown requires only three molecules of the types RCHO, NO, HC and two solar photons ($h\nu_1$ and $h\nu_2$). Perhaps the most interesting species of figure 1 from a chemical standpoint is ozone (O_3). Ozone is not directly emitted from sources but is produced and destroyed by a very complicated series of chemical reactions among and with its precursors. As a result of this complexity, the precursor-product relationships for ozone and other chemicals involved in atmospheric oxidation cycles are not straightforward, although many of the individual reactions have now been studied. The basic equations involved in tropospheric creation and destruction are



¹Much of the work discussed herein was done in collaboration with the author's colleagues at Bell Laboratories: W. S. Cleveland, D. Edelson, L. A. Farrow, R. S. Freund, B. Kleiner, K. B. McAfee, and T. A. Weber.



where M signifies a third body which acts to stabilize the reaction. The first equation demonstrates that solar radiation ($h\nu$) is required for ozone formation; the third that ozone destruction by NO is a direct process. Since NO is the principal oxide of nitrogen emitted by combustion sources, ozone is preferentially removed near strong combustion sources and preferentially formed by oxidized products when away from those sources. In addition to the effects of NO and NO₂, it has been surmised that hydrocarbon emissions could affect ozone concentrations, since peroxy radicals (RO₂•) of the hydrocarbons provide a means for oxidizing NO to NO₂ without the ozone loss involved in reaction (3):



Calculational results pertaining to this topic will be discussed later in this paper.

Most of the products of urban photochemistry do not appear to be subject to the cyclic oxidation-reduction sequences characteristic of ozone. Rather, their reactions proceed unremittingly in the direction of further oxidation, forming low-vapor-pressure compounds whose fate is likely to be deposition on aerosols or on boundary-layer surfaces. Some of these chains are shown in figure 2. Emission of the precursors SO₂, NO, and hydrocarbons (HC) is followed by initial oxidation, largely through free-radical reactions. (The reactions shown are specific in the cases of SO₂ and NO but merely representative of typical processes for the chemically diverse hydrocarbon compounds.) A second oxidation step, which may also be through a free-radical process, produces inorganic acids from the inorganic precursors. For the organic species, the reaction chains are longer and the products more numerous; acrolein and peroxyacetyl nitrate (PAN), as shown in figure 2, are among the products. More detailed discussions of organic chemical chains in urban atmospheres are given by Demerjian et al. (ref. 2), the Panel on Vapor-Phase Organic Pollutants (ref. 3), Graedel et al. (ref. 4), and Heicklen (ref. 5).

The four subdivisions of figure 2 provide a useful insight into the present status of atmospheric measurement capabilities. Many of the emittants have been extensively measured at a variety of tropospheric locations; thus, information on their emission fluxes and ambient lifetimes is available. For relatively unreactive species, of which carbon monoxide is perhaps the prime example, the measurements serve in addition as tracers of meteorological transport and diffusion processes.

The initial oxidation products of figure 2 have a diverse measurement status. Nitrogen dioxide (NO₂) is widely monitored; the remainder have been seldom or never detected (in part because of their high reactivity and short lifetimes). The final oxidation products have been measured infrequently. The same is true of the chemical constituents of aerosols.

Thus, it is possible to categorize the species of figure 2 (and other similar species not shown) as potentially providing insight into (1) emission and dispersion of trace atmospheric constituents, (2) initial chemical reactions, (3) final products of gas-phase chemical chains, and (4) products of gas-aerosol

interactions. The successful description of each of these processes is required for a comprehensive understanding of the chemistry of the urban troposphere.

KINETIC PHOTOCHEMICAL MODELS

The details of urban photochemistry involve the complex and time-varying interplay of chemical kinetics, contaminant emissions, and bulk airflow. Modeling of these processes thus requires appropriate descriptions of both chemistry and meteorology and of the nonchemical source and sink processes that are involved. The calculations to be described in this paper are primarily intended to study the chemical details. For this reason, a large reaction set has been constructed which can yield information about many minor constituents as well as provide calculated curves for comparison with data on those species for which measurements have been made. This set consists of 143 reactions in 76 species and has been presented by Graedel et al. (ref. 4). It includes extensive descriptions of O-H-N and sulfur chemistry, together with a representation of the chemistry of atmospheric hydrocarbons and their products. The organic compounds that are specifically treated are methane, ethane, propylene, and the aliphatic aldehydes. In addition to the commonly measured emittants and products, the chemical set treats specifically a number of photochemical products of relatively low vapor pressure: the inorganic acids HNO_3 and H_2SO_4 , the organic acids HCOOH and CH_3COOH , the alcohols CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$, a number of organic nitrates, and a variety of other species.

The interactions of aerosols and gases in the atmosphere are imperfectly understood yet are vital to a complete description of urban photochemistry. Although the techniques for including an assessment of these interactions in a computational representation of the troposphere are not well developed, a key to inclusion of heterogeneous atmospheric chemistry is the realization that pure inert solid particles may be a rarity in the atmosphere and that the chemically inert particle core is in most or all cases surrounded by a hygroscopic layer (Winkler (ref. 6)). This layer, upon contact with water vapor, will form a solution with an equilibrium vapor pressure suitably depressed from that of pure water so that the aqueous layer is stable. Thus, atmospheric aerosols may be accurately represented as solid core particles with water shells (perhaps only a few monolayers thick during low humidity) rather than as particles with solid surfaces. The functional result of this deduction is that the aerosol-gas interaction may be treated by gas-liquid, as opposed to gas-solid, interface techniques. Graedel et al. (ref. 7) have established that the amounts of stable atmospheric gases absorbed in the aerosol are negligible fractions of the total gas-phase concentrations and can thus be neglected for atmospheric chemical purposes (but not necessarily for considerations of the chemistry within the aerosols themselves). The interactions between radicals and water-covered aerosols are likely to be substantially more efficient than the interactions between free radicals and stable gases. It appears certain that the inorganic radicals, such as $\text{HO}_2\cdot$ and $\text{HO}\cdot$, will be instantly absorbed on impact; this is also extremely likely for other radicals. In this initial formulation, therefore, it has been assumed that all radicals will be absorbed into aerosols on impact, a conclusion that has been reached independently by Warneck (ref. 8). The resulting concept for aerosol-gas interaction is indicated in figure 3.

The computational architecture that is utilized to represent northern New Jersey is based on a matrix of geographical areas in which each matrix element is a rectangularized transformation of the dimensions of a county. The flow of gases from one matrix element to the next is controlled by the local wind velocity and direction. In the computations discussed here, an average diurnal wind flow pattern derived from measurements at Newark Airport (Essex County) on summer days of normal convective mixing has been used. The variations in mixing height are specified by a function derived from lidar measurements of the atmospheric aerosol. The chemical species within each reaction volume are assumed to be fully mixed.

Inventories for emission of trace contaminants have been compiled on a countywide basis. Each of the counties is thus treated as a "reaction volume" with source terms corresponding to the emission data. Emissions attributable to mobile sources are varied in accordance with local traffic density functions, and those for power plants in accordance with energy generation patterns. Other emissions are regarded as constant with time.

The elements utilized in the computations are (from west to east, in the typical direction of the summer wind flow and that used in the calculations) Morris County (a semirural county with low anthropogenic emissions), Essex County (a suburban county with moderate anthropogenic emissions), and Hudson County (an urban county with high anthropogenic emissions). A schematic diagram of this meteorological and geographical approach is shown in figure 4.

URBAN PHOTOCHEMISTRY

Workdays

Computations representing the chemistry of the troposphere on sunny summer workdays with westerly wind flow have been carried out for Morris, Essex, and Hudson Counties and the results for Hudson County compared with an extensive set of air quality data from a monitoring site in Bayonne (Hudson County). The data values that result for O_3 , NO, NO_2 , and SO_2 are plotted in figure 5, together with the diurnal concentration patterns resulting from the calculations. The computed diurnal curve for NO demonstrates good time coincidence with the measured peak and therefore indicates the general appropriateness of the emission terms in the computation and the NO removal reactions in the chemical set. NO_2 decreases at sunrise as the volume of the mixed layer rapidly increases. The principal NO removal paths involve oxidation to NO_2 , and it is therefore satisfying to find a 9 a.m. NO_2 peak with temporal agreement between computations and measurements. The computations also reproduce the NO_2 increase following sunset, which reflects both the lowered depth of the mixed layer and the absence of NO_2 photodissociation. The results of the model for the hours following sunset appear to be too low for both NO and NO_2 . This occurs because of the gradual termination of the vigorous mixing conditions that were prevalent in the sunlit hours. The ground-level measurements thus reflect the ground-level concentrations to a greater degree than the altitude-averaged concentrations of the model.

The best evidence for the general correctness of the extensive chemical model is provided by the diurnal curves for ozone. Although the patterns differ slightly, both show the afternoon peak typical of measured ozone values, and their integrated diurnal concentrations (i.e., the total amount of ozone that is created) are similar.

One of the characteristic daily patterns of the photochemical smog sequence is the existence of sequential concentration peaks of NO, NO₂, and O₃ (e.g., U.S. Environmental Protection Agency (ref. 9)). This pattern has recently been confirmed for data from northern New Jersey (Cleveland et al. (ref. 10)). Figure 5 demonstrates that such a pattern is also a feature of the computational results.

The computed diurnal variation for the SO₂ concentration follows the observed concentration pattern closely and exceeds the observed mean values by about a factor of 2. Conversion of SO₂ to sulfate in the atmosphere is fairly rapid, however, and a large portion of this conversion may be catalyzed by aerosols from the SO₂ dissolved in them. In the absence of sufficient experimental data to permit kinetic studies of interior aerosol chemistry, it is impossible to calculate the magnitude of such an effect. In lieu of such an approach, however, the "sticking coefficient" between SO₂ and aerosol surfaces that would be required for the diurnal calculations to reproduce the observed SO₂ concentration data has been calculated. Since additional gas-phase removal mechanisms for SO₂ may, of course, be important, the resulting sticking coefficient is appropriately regarded as an upper limit to the true number. The required value is 0.05; that is, 5 of every 100 gas kinetic collisions between SO₂ molecules and aerosol surfaces result in SO₂ incorporation into the liquid surface layer of the aerosol.

Computational results are available not only for the total diurnal behavior of the major species shown in figure 5 but also for a spectrum of secondary species. In several cases, their concentrations can be compared with measurements in northern New Jersey or elsewhere (refs. 11 to 14). These comparisons, shown in table I, confirm in more detail the basic validity of the model, although for species measured outside New Jersey the comparison must be regarded as an order-of-magnitude confirmation. Nonetheless, the good agreement between the computed and measured concentrations and diurnal patterns for both primary and secondary trace species indicates that the model formulation contains the essence of the chemical and meteorological processes that occur in the urban atmosphere of northern New Jersey.

The results of the urban workday computation have been discussed in detail by Graedel et al. (ref. 4); the discussion need not be repeated here. It is appropriate, however, to list some of the most important conclusions of the work:

(1) Free-radical reactions are of vital importance for many chemical processes in the urban atmosphere. The oxidation of olefins, for example, is controlled by initial reactions with the hydroxyl radical. The computed peak concentrations of important free radicals have been predicted: HO₂•, 6×10^8 molecules-cm⁻³; CH₃O₂•, 1×10^8 molecules-cm⁻³; HO•, 1×10^6 molecules-cm⁻³.

(2) The aliphatic aldehydes occupy central positions in many chemical chains. They provide the primary urban source for the reactive free radicals and are precursors to such important toxic products as PAN.

(3) The effects of sulfur chemistry on the overall gas-phase chemistry of the urban troposphere do not appear to be of major importance (see also Graedel (ref. 15)). The major influence is the scavenging of odd hydrogen radicals ($\text{HO}\cdot$ and $\text{HO}_2\cdot$) by SO_2 . The importance of oxidized sulfur compounds to aerosol chemistry has not been adequately assessed; however, they may be much more important in that chemical regime.

Sundays

Recent statistical investigations of air quality data have clearly disclosed a tendency for similar average ozone levels on summer Sundays and workdays, despite markedly different traffic patterns (Bruntz et al. (ref. 16) and Cleveland et al. (ref. 17)). The complex relationships among ozone, a photochemical product, and NO , NO_2 , and hydrocarbons, its supposed precursors, have thus been demonstrated to be highly nonlinear. To investigate this situation, the urban workday computation just described is modified to allow a simulation of urban atmospheric chemistry on Sundays. The most important change is the marked difference in motor vehicle emission and power generation functions. Atmospheric aerosol concentrations are lower on Sundays and, perhaps as a result, the solar radiation at ground level is somewhat higher (Cleveland et al. (ref. 17)). In addition to its meteorological effects, the change in aerosol concentration reduces the heterogeneous interactions which affect tropospheric chemistry (Farrow et al. (ref. 18) and Graedel et al. (ref. 7)). The increased solar radiation increases the rate of the photosensitive reactions included in the chemical set.

The diurnal concentration patterns for O_3 , NO , and NO_2 for the workday and Sunday calculations are shown in figure 6. The Sunday calculation reproduces two important characteristics of the Sunday ozone data illustrated by Bruntz et al. (ref. 16): the virtual equivalence of the afternoon ozone peak and the higher ozone values on Sunday morning. The calculation demonstrates higher Sunday evening values not reflected in the data; this discrepancy may be a result of inadequate representation of the heavy traffic flow from New Jersey shore points into the metropolitan area that occurs on summer Sunday evenings.

The rather complex analytical techniques used to interpret the urban Sunday calculations have been presented elsewhere (Graedel (ref. 19) and Graedel et al. (ref. 20)). Their use demonstrates that the near equivalence in urban ozone concentrations on workdays and Sundays results from the near workday-Sunday equivalence of the following factors: tight balance between ozone production through NO_2 photodissociation and ozone scavenging by NO (reactions (1) and (3)), the advection of ozone from less urban areas, and the incorporation of similar quantities of ozone preexisting above the morning mixed layer. The higher levels of NO_2 on workdays increase the rates of the NO - NO_2 - O_3 shuttle reactions but do not significantly alter the similar behavior of odd oxygen on workdays and Sundays. The increased levels of oxides of nitrogen on workdays have other consequences, however. The advective transport of NO_x is somewhat enhanced relative

to Sundays, with a concomitant expansion of the downwind impact of the urban area. In addition, the rates of secondary reactions are higher on workdays, resulting in higher concentrations of organic and inorganic nitrates and concomitant increases in the potential of the atmosphere to cause lachrymation.

AIR TRANSPORT AND AIR QUALITY

The transport of urban air over long distances and its subsequent influence on downwind air quality have been deduced for several years in data from the Los Angeles basin (Altshuller (ref. 21)). More recent investigations have demonstrated that urban plume effects are seen in other geographical areas as well. An example of such work by Cleveland et al. (ref. 22) is shown in figure 7, which illustrates ozone concentrations at different times of day for air monitoring sites throughout the Northeastern United States. The prevailing wind on the day in question was from the southwest (i.e., from Washington, D.C., to Boston). The high ozone concentrations demonstrate the transport of urban air across this region, the peak levels in northern Massachusetts actually occurring after sunset when photochemical ozone production has ceased.

Other trace constituents in the air are also subject to transport effects. The dependence of total particulate matter in Greenwich, Connecticut, on prevailing wind direction is illustrated in figure 8 taken from Bruckman (ref. 23). This particulate matter almost certainly contains both physically and chemically produced components (Cunningham et al. (ref. 24) and Grosjean and Friedlander (ref. 25)) and is thus directly related to studies of chemical precursors and products. Similar results for sulfate aerosol throughout the Northeastern United States have been presented by Lioy et al. (ref. 26).

Photochemical calculations investigating the interesting and important effects of transport on air quality on subcontinental size scales have yet to be performed. On a less ambitious scale, however, the air quality upwind of, within, and downwind of urban areas in northern New Jersey has been modeled by expanding the geographical regime of figure 4. The size of the computational matrix was increased to 6×1 by adding three representative but fictitious counties downwind of the three to which the previous results apply. This procedure was followed because the actual counties downwind of Hudson County (New York City and Long Island and adjacent waters) are associated with certain meteorologically complicating factors, such as the Manhattan "heat island" and the land-sea interfaces with Long Island Sound and the Atlantic Ocean. Such manifestations would interfere with any straightforward examination of the chemical processes and have been avoided. The resulting computational sequence is shown in figure 9. The three added counties are given descriptive names for convenience in referencing: Shopview (emissions flux equal to Essex County without power plants), Deerfield (emissions flux set to estimated natural rates), and Farmland (emissions flux set to estimated natural rates).

The computed peak concentrations of NO , NO_2 , and O_3 for normal emission fluxes are presented in figure 10 for the six-county sequence. As in previous work, the results apply to sunny summer days with west winds of average speed. Two features are immediately apparent: the ozone decrease as the urban area is approached from upwind and the subsequent increase downwind of the urban area.

The effects of advection are also seen, since the flow of oxides of nitrogen from Hudson County results in the highest NO and NO₂ peaks and the lowest O₃ peak occurring in Shopview County, an area of lower emission rates. Further downwind, the effects of dilution and decreased emissions outweigh those of advection. This is consistent with the observation that ozone concentrations in regions of high emission rates are lower than in surrounding, less urban areas (e.g., Spicer (ref. 27)).

For photochemical products other than ozone, it seems appropriate to examine the concentrations at 7 p.m., by which time the bulk of the precursor emissions and product reactions have occurred. Figure 11 shows the concentration behavior of C₃H₆, NO₂, SO₂, and four photochemical products - acrolein, nitric acid, PAN, and SO_x⁻². SO_x⁻² is defined as H₂SO₄ + HSO₃·, since the present computational formulation does not treat the ultimate fate of the HSO₃· radical. (SO_x⁻² is regarded as essentially equal to gas-phase sulfate.) The progression of SO₂ oxidation with downwind distance is readily apparent, the SO_x⁻² concentration increasing from 0.4 ppb in Morris County to 1.5 ppb, 125 km downwind. Similar but somewhat less dramatic behavior is shown by nitric acid, PAN (CH₃C(O)O₂NO₂), and acrolein. The impact of these photochemical products is thus felt not principally in the urban area from which the precursors originate but in the downwind areas within the urban plume. Additional results and chemical analyses are presented by Graedel et al. (ref. 28).

OVERWATER TRANSPORT OF URBAN AIR

Recent observations at shoreline sites downwind and overwater from urban areas have shown enhanced ozone concentrations when the predominant wind direction is from the urban area to the site (Graedel and Farrow (ref. 29)). This result suggests a further manifestation of the interplay between atmospheric chemistry and meteorology, since ozone undoubtedly represents in some sense the family of photochemically produced species. To investigate the overwater transport situation computationally, the six-county sequence of figure 9 is modified by replacing the fourth region (Shopview County) in the overland downwind case by a traverse overwater (Aqua County) during which no emissions of hydrocarbons or nitric oxides occur (fig. 12). The resulting concentrations and rates are then analyzed for Shopview and Aqua Counties and for the counties further downwind. The peak ozone concentrations calculated for both the overland and the overwater traverses are shown in figure 13. It is readily apparent that the enhanced ozone levels observed in air quality data following overwater transport are reproduced by the calculations. The computed enhancements are 7 percent in Aqua County (in comparison with Shopview County), 3 percent in Deerfield County, and 1 percent in Farmland County.

The presence of enhanced photochemical activity during the overwater traverse suggests that chemical product formation as well as ozone concentrations may be enhanced in comparison with those of the overland case. To investigate this hypothesis, three pairs of precursors and products have been examined: NO₂ and HNO₃, SO₂ and gaseous sulfate (H₂SO₄ + HSO₃·), and C₃H₆ and PAN. In figure 14, the ratios of products to precursors at 7 p.m. are plotted for six-county overland and overwater traverses. The results indeed indicate increased photochemical processing during overwater transport. The largest change occurs

in the sulfate conversion ratio, which is 51 percent higher in Aqua County than in Shopview County. Further downwind, however, the influence of the overwater transport diminishes to ≤ 10 percent of the conversion ratios. The overwater transport has thus caused local but not enduring changes in the conversion ratios of the photochemical products.

As air that has been involved in an overwater traverse again encounters land areas with significant anthropogenic emissions, the NO_2/NO concentration ratio adjusts to a balance between the overland sources and sinks of oxides of nitrogen. This adjustment is reflected in a gradual approach of the concentrations of the chemical species to the conditions obtained under overland traverses. In these calculations, the recovery of the air parcel from overwater transport is much less rapid than is its response to the initial perturbation, because the emission density of Shopview County is much higher than that of Deerfield County. Reestablishment of the unperturbed chemistry of the overland traverse is hence not specified completely in the overwater calculations, which are able to follow the air parcels only limited distances downwind. It appears, however, that the long-range effects of brief overwater traverses in a chiefly overland trajectory will be small and that the total integrated emissions inventory will be the dominant influence on the atmospheric chemical product concentrations in locations far downwind of urban areas.

EMISSION VARIATIONS IN THE URBAN ENVIRONMENT

The success of model calculations in reproducing a wide variety of field data suggests that calculations may also be used to predict the effects of significant changes in the emission rates of selected gaseous species. This approach has been used in the northern New Jersey calculations to study the potential effects of large changes in NO and hydrocarbon (HC) emission rates. Calculations with altered source strengths are accomplished as follows. In each county, the normal summer rates for the emission of trace contaminants are established. Variations in source strength are then treated as fractional changes to the basic rates; diurnal emission patterns are retained. The calculations are thus equivalent to source alterations applied on a uniform percentage basis. All calculations utilize the meteorological conditions that have been described previously.

Two sets of computational experiments have been performed for the six-county sequence of figure 9. One set examines the air quality resulting from different NO emission fluxes at constant HC emission flux. The second utilizes different HC emission fluxes at constant NO emission flux. The differences are readily demonstrated by plotting the diurnal peak ozone values for different computations as a function of downwind distance (fig. 15).

The "ozone shield" set up by dense urban areas is illustrated by the Hudson County values, where increases in NO emission rates are seen to decrease peak ozone values by as much as 15 percent, for the cases studied here. Increases in HC emissions cause increases in the ozone maxima but the magnitudes are very small (≤ 3 percent for a threefold emissions increase). These effects are consistent with predictions by Dimitriadis (ref. 30) based on smog chamber experiments and with the smog chamber modeling results of Hecht (ref. 31) and Lawrence

Livermore Laboratory (ref. 32) for non-methane hydrocarbon/ NO_x ratios typical of urban conditions.

The interrelationships between precursors and products may be studied by examining the product concentrations in a single location as the precursor emission rates are varied. The left side of figure 16 shows the resulting product concentrations in Hudson County at 7 p.m. for computations in which the HC emission rates in the several counties were varied relative to the best current source estimate (1.0 on the abscissa); NO emission rates were held constant. In addition to the gas-phase species, the heterogeneous aerosol mass gain resulting from accretion of low-vapor-pressure compounds (TPM) is included. The effects of HC emission variation on all species, even for those products that are primarily organic in nature, are seen to be no larger than 2 percent for changes in HC emission as large as a factor-of-2 decrease or a factor-of-1.5 increase.

Photochemical product concentrations for computations in which the NO emission rates were varied and the HC rates held constant are shown on the right side of figure 16. Here the concentration changes of the photochemical products are substantial. Although the magnitudes of the effects differ, in every case a reduction in NO emissions produces a concomitant decrease in the photochemical product. The concentration variations of other photochemical product species included in the computations are similar.

The trends of O_3 , NO, and NO_2 concentrations discussed in this paper suggest that the increase in ozone concentrations in the downwind suburban and rural counties is coincident with an increase in the ratio of the peak values of NO_2 and NO. This "photostationary state" condition (Stedman and Jackson (ref. 33)) is seen in all of the computed results. This is shown in figure 17 where the ozone maxima for all of the six-county overland calculations are plotted as a function of the NO_2/NO concentration ratio at noon. The relationship is nearly linear over the very wide range of urban density and emission flux utilized in the calculations. This suggests that the effects of changes in emission fluxes on ozone concentrations, at least in the northern New Jersey region and for the conditions represented by the calculations, can be assessed by answering the question, "How will the change perturb the NO_2/NO ratio?" For example, an increase in the NO emission flux will decrease the ratio locally but may allow for increased NO oxidation and an increased ratio downwind. The ozone maxima will follow these changes.

For many of the photochemical products discussed herein, the interactions of the hydroxyl radical turn out to be quite important (e.g., Davis et al. (ref. 34) and fig. 2 of this work). This circumstance renders the reaction



doubly significant, since it is the principal source of hydroxyl radicals in the urban atmosphere (Graedel et al. (ref. 4)). This dependence is demonstrated by figure 18, in which the relationship between NO_2 and $\text{HO}\cdot$ (Farrow and Graedel (ref. 35)) for all of the six-county computations is shown. The very slight dependence of any of the photochemical products on hydrocarbon emission appears to be due to the natural background of hydrocarbons throughout the region (and most of the continental United States) and to the central position of reac-

tion (5) as a rate-limiting step for much of the free-radical chemistry of the atmosphere. In a qualitative sense, these results may be generally applicable to urban atmospheres in which incoming air has encountered predominantly over-land traverses. Regardless of the particular spectrum of urban hydrocarbons, each hydrocarbon compound will react predominantly with HO \cdot (e.g., Gorse and Volman (ref. 36) and Hansen et al. (ref. 37)). Since the formation of oxygenated products in all currently proposed atmospheric sequences involves oxygen abstraction and/or NO $_x$ addition and since NO $_x$ is the principal oxygen abstractor in the troposphere, it appears that virtually all atmospheric photochemical products will be responsive to ambient concentrations of NO $_x$, at least in the urban atmospheres where the radical sources and sinks are dominated by NO $_x$ reactions.

The implications of these results are substantial ones for tropospheric chemistry and it is thus important that the limits to their generality be firmly stated. First, it is cautioned that, although the computational results are in reasonable agreement with air quality data for workdays and Sundays and for the case of overwater transport, the comparisons apply to the specific conditions of full sun, westerly wind flow, and simplified treatment of the applicable meteorology. A further limitation is the accuracy of the hydrocarbon emissions inventory, which is probably no better than ± 25 percent. The minimal response of photochemical product formation to large hydrocarbon emission variations ameliorates that problem to a great extent, however. While the conclusions appear to reflect a basic understanding of the atmospheric processes that occur, the results cannot be quantitatively applied to arbitrary geographical areas with arbitrary meteorological situations. In particular, the treatment of urban meteorology is insufficient to predict in detail the behavior of atmospheric chemistry during "episode" periods, when winds are low or calm and when mixing is much reduced.

SOURCES OF ERROR IN URBAN PHOTOCHEMICAL COMPUTATIONS

The complex and extensive data required to formulate an atmospheric model are inherently limited in precision and accuracy. It is therefore of substantial interest to assess the effects of inaccurate specification of the various parameters on the computational results. Although it is possible in principle to study the maximum perturbation of an individual computational output produced by variation of all the input parameters within their estimated error limits (e.g., Cukier et al. (ref. 38)), such techniques are not tractable for computations of the complexity dealt with here. One can perform computational experiments, however, in which selected individual parameters or groups of parameters are varied within their error limits. While the results cannot be said to define the "sensitivity" of the computation in a mathematically precise way, they provide approximate bounds to the accuracy of the computation if the variational experiments are carefully chosen (Duewer et al. (ref. 39)). In this section, a variety of such experiments with the Bell Laboratories model are described and the results assessed.

Incomplete Chemical Formulation

The spectrum of compounds in urban air is so large that a complete formulation of the chemical reaction chains would involve thousands of reactions, the majority of which would have undefined rate constants, products, or both. A drastic condensation of this "ultimate" reaction set is thus necessary if models are to be constructed. The condensation inevitably involves personal judgments as to the degree of complexity required for effective simulation of the real system and the degree to which unmeasured reaction parameters can be estimated.

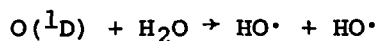
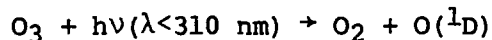
The major condensation in most tropospheric models is made with the organic chemical reactions. Although scores of hydrocarbons are commonly measured in urban air (e.g., Altshuller et al. (ref. 40) and Grob and Grob (ref. 41)), most of the carbon atoms present are contained in perhaps a dozen compounds. The tendency of hydrocarbon chains to produce identical fragment products suggests that careful treatment of these principal species may suffice for all practical purposes. Even this restricted goal seems intractable at present, however, because of the deficiencies in laboratory and field data (particularly for the aromatic compounds). A further consideration is that emission inventories for urban areas do not generally subdivide hydrocarbon emissions by species; thus, there is the danger that a complete chemical treatment will be coupled with a totally insufficient set of boundary conditions.

The choice made in the Bell Laboratories model for representation of organic chemistry has been to restrict the treatment of hydrocarbons to methane, ethane, propylene, formaldehyde, acetaldehyde, and their reaction products. Source emissions are subdivided according to experimental species determinations from representative emission sources. Methane and, to a lesser extent, ethane are moderately reactive species and have important global chemical roles in addition to their participation in urban chemistry. The use of propylene to represent the spectrum of reactive compounds provides access to the singly bonded two-carbon group and the one-carbon fragment necessary for the production of many of the compounds and radicals (e.g., CH_3CHO , HO_2^\cdot , $\text{CH}_3\text{C}(\text{O})^\cdot$) thought to be chemically important (Leighton (ref. 42), Demerjian et al. (ref. 2), and Morris and Niki (ref. 43)). Nonetheless, the limitation of hydrocarbon chemistry in this way prevents the computation from providing information on many organic atmospheric products of interest, and thus, the computation cannot be regarded as a total representation of atmospheric chemical processes. Perhaps the best assessment that can be made of its general utility is the comparison of measured and computed concentrations of selected products of the organic chemistry. This comparison (table I) suggests that the current organic formulation is a reasonable one.

The chemistry of atmospheric sulfur is poorly defined at present (Davis and Klauber (ref. 44) and Graedel (ref. 45)). The initial loss reactions are well known, however, so that the effects of SO_2 on HO^\cdot and HO_2^\cdot (the principal scavenging species) can be calculated. The effects of the optional chemical paths for the oxidized sulfur products on the overall chemistry have been explored in a series of sensitivity studies (Graedel (ref. 15)). It was concluded that while a full and accurate treatment of urban gas-phase sulfur chemistry is doubtless required for assessments of the atmospheric sulfur cycle,

such a treatment is not crucial to the accurate representation of the chemistry of non-sulfur compounds.

In nonurban atmospheres, the primary source of the important hydroxyl radicals is thought to be (Crutzen (ref. 46))



In urban atmospheres, however, the principal source is (Graedel et al. (ref. 4))



where the $\text{HO}_2\cdot$ comes from aldehyde photolysis. The importance of including $\text{O}(^1\text{D})$ chemistry in urban calculations has been assessed by a calculation omitting its sources and sinks (Graedel et al. (ref. 4)). The results demonstrated that the $\text{O}(^1\text{D})$ chemistry was indeed of significance, primarily because it represents a pure source of odd hydrogen radicals rather than a reshuffling of existing ones.

Heterogeneous processes (i.e., the interaction of gas-phase molecules with atmospheric aerosols and with ground surfaces) are not well understood. The treatment adopted herein has been discussed in the section "Kinetic Photochemical Models;" it is clearly a preliminary formulation. The inclusion of such effects in the urban kinetic computations has been investigated at some length (Farrow et al. (ref. 18) and Graedel et al. (refs. 4 and 7)), and it has been concluded that the processes are significant but not dominant for substances (e.g., $\text{HO}\cdot$ and $\text{HO}_2\cdot$) with very short chemical lifetimes. For more stable species, particularly photochemical products of low vapor pressure such as HNO_3 , H_2SO_4 , and $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$, surface removal is the principal loss mechanism. The inclusion of surface effects in a chemically consistent manner is thus an important goal for studies of the cycles of these product species. It appears that the reactions of compounds containing only oxygen, hydrogen, and nitrogen are treated with sufficient comprehensiveness in the present formulation of the urban model. An exception that might be noted is that the chemistry of ammonia is not included. Ammonia's gas-phase processes are not rapid, however (Graedel (ref. 47)), and it appears that the atmospheric chemical cycles of ammonia are principally heterogeneous (Charlson et al. (ref. 48)). Therefore, its omission has little potential effect on gas-phase processes.

A variety of organic (Glasson and Heuss (ref. 49)) and sulfoxyl (Calvert (ref. 50)) nitrates are likely to be formed in urban atmospheres. The present information about such compounds is sketchy. If present, they will be chemical end products rather than reactive intermediates; this property makes it unlikely that their omission will significantly perturb other aspects of urban photochemistry. The work described here treats PAN and other organic nitrogen-containing compounds whose chemistry appears to be reasonably well specified.

As has been discussed by Duewer et al. (ref. 39) for the case of stratospheric models, one cannot exclude the possibility of an important chemical

process being omitted from these chemical calculations. It is possible, however, to justify the inclusion of specific processes (as has been done in this paper in several cases). There appears to be good evidence that the current treatment includes the reaction paths of major tropospheric significance. Nonetheless, knowledge of the chemistry of specific organic groups (such as the aromatic compounds) and of heterogeneous processes is inadequate or nonexistent at present. For products or processes where these deficiencies are important, much additional information is obviously needed.

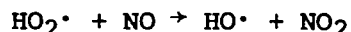
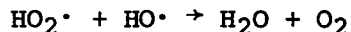
Inaccurate Rate Parameters and Incorrect Products

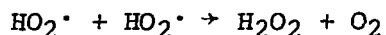
Four types of processes occur in tropospheric gas-phase chemistry: molecule-molecule reactions, molecule-radical reactions, radical-radical reactions, and unimolecular processes (of which photodissociation is the most important example). In the first case, laboratory techniques are relatively straightforward and rate parameters and product determinations appear to be satisfactory. Molecule-radical reactions receive a mixed assessment. The two most important tropospheric radicals are $\text{HO}\cdot$ and $\text{HO}_2\cdot$. The former can be satisfactorily handled in the laboratory and most of its molecular reaction parameters appear to be sufficiently well determined. $\text{HO}_2\cdot$, on the other hand, is difficult to generate and measure in analytically tractable laboratory systems. Fortunately, the number of tropospheric reactions in which $\text{HO}_2\cdot$ enters is much smaller than for $\text{HO}\cdot$, and good progress is being made on laboratory techniques for $\text{HO}_2\cdot$ kinetics.

Radical-radical reactions are very hard to study in laboratory systems. Further, they have been shown to be of great importance in stratospheric chemical cycles. The situation is much less severe in the urban troposphere, because the presence of relatively high concentrations of reactive molecules and aerosols and the proximity of ground surfaces increase alternate loss processes greatly.

Some uncertainties exist in the specification of quantum yields and products for photodissociation reactions. The quantum yield results must be obtained in such a way that collisional quenching at 1 atmosphere of pressure is appropriately included; this is sometimes a difficult requirement. Consideration of the variations in quantum yield with temperature, which is important for models with wide altitude ranges, is not of consequence in urban calculations.

The specific reactions in which inaccuracies in the rate parameters may be reflected strongly in the computational output are thought to be

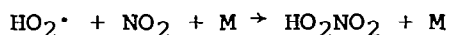




As may be seen at once, HO_2^\cdot is involved as a reactant in each. The effects of a change of 1 order of magnitude in the rate constant for the first reaction have been specifically assessed (Graedel et al. (ref. 4)); they were minimal because of the predominance of competing reactions for both species. The last reaction, for which the error limits in the rate constant are much tighter (Hampson and Garvin (ref. 51)), is expected to behave similarly. The rate constant for $\text{HO}_2^\cdot + \text{NO}$ has recently been remeasured (Howard and Evenson (ref. 52)) to be about a factor of 40 larger than the previously accepted value (Hampson and Garvin (ref. 51)). Sensitivity studies of the effect of this change are in progress.

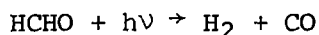
Any uncertainties in the rate parameter for $\text{HO}_2^\cdot + \text{O}_3$ appear unlikely to influence urban chemistry very much. The effect of the reaction is twofold: it reduces HO_2^\cdot to HO^\cdot and it provides an ozone sink. The first process is also accomplished by $\text{HO}_2^\cdot + \text{NO}$, a reaction which has a rate 35 times as great as $\text{HO}_2^\cdot + \text{O}_3$, even at 1975 rate constant values. The latter process is much less important as an ozone sink than many competing reactions, such as the scavenging of ozone by the olefins.

The formation of pernitric acid by the reaction



has recently been confirmed (Levine et al. (ref. 53) and Niki et al. (ref. 54)). It appears that thermal dissociation of the product is rapid enough so that this process should be unimportant (Pitts, private communication, 1977); nonetheless, a calculational assessment of its influence is underway.

Of the photodissociation reactions in the urban atmosphere, those of formaldehyde are perhaps of the greatest present concern:



Some complexities in measured values (Calvert et al. (ref. 55), Houston and Moore (ref. 56), and Lewis et al. (ref. 57)) make specification of both the total quantum yields and the branching ratios for these processes uncertain. A related problem is the specification of the chemical rates of the CHO^\cdot radical (Osif and Heicklen (ref. 58) and Niki et al. (ref. 59)). The effects of these uncertainties are being studied in calculations now underway.

Since the rate of any bimolecular reaction



is given by the product of the concentrations of its reactants and its rate constant

$$R = k[A][B]$$

the effects on a chemical system of a factor-of-2 uncertainty in the rate constant can be assessed either by changing k or by changing the concentrations of one of the reactants. From this standpoint, the emission variation studies described in the section "Emission Variations in the Urban Environment" can be looked upon as sensitivity studies of groups of reactions. Since changes of a factor of 2 in the spectrum of hydrocarbon compound emissions perturbed the basic chemical system to only a small degree, the sensitivity of the urban model to rate parameter inaccuracies affecting the hydrocarbons may be inferred to be small. This is not true for nitric oxide, for which emission variations resulted in substantial differences in the computed results. The uncertainty in the rate parameters for the oxides of nitrogen is of the same order of magnitude as for hydrocarbons (Hampson and Garvin (ref. 51)). Thus, the emission variation calculations provide no sensitivity analysis for the NO_x chemistry, which is best assessed by the individual reaction studies already discussed.

Solar Insolation Values

Many of the important reactions in urban chemistry involve solar photons; thus, an imprecise specification of the photon flux is of potential concern. Solar insolation is location and time dependent, unlike the chemical formulation and specification of reaction parameters. One must therefore interpret solar insolation accuracy as a function of the goals of the model. If one wishes to simulate a particular day in a given location, insolation measurements for that situation must be provided. If an average air quality for selected days or seasons is desired, the measurements must be appropriate to those goals. In principle, solar insolation can be measured with accuracies better than 1 percent (Marchgraber (ref. 60)), and a significant error in the computational results can thus be avoided with careful attention to field data.

Although computational errors due to poor insolation specification can be avoided, it is of interest to assess the sensitivity of the photochemistry to changes in insolation resulting from variations in solar zenith angle, clouds, aerosols, and so forth. In the case of photosensitive species such as ozone, model calculations have shown that the imposition of full cloud cover on a summer workday in New Jersey can cause concentration decreases of greater than a factor of 10 (Graedel et al. (ref. 61)). Similar results have been presented by Peterson and Demerjian (ref. 62). It is apparent that modeling of air quality processes at a specific time and place will require accurate photon flux information. Modeling efforts with didactic or prognostic goals, however, can be adequately achieved with specification of average or typical solar flux values.

Background Concentrations

The concentrations of trace species in the air entering an urban region are quite significant to the subsequent chemistry. For most species, these background concentrations are lower than those within the urban area and the advected air tends to cleanse the urban atmosphere. For ozone the situation is often reversed; advection is thus a net source.

The background concentrations are, in general, poorly established. The exception again is ozone, for which extensive data are now available for the Northeastern United States. For other species, it is necessary to rely on less detailed measurements. In modeling specific days, one is thus often presented with boundary conditions that are not defined by field observations. Calculations representing typical conditions, however, are less likely to be strongly influenced by boundary factors. This is particularly true if qualitative interpretations rather than quantitative predictions are desired. In the former case, it is perhaps sufficient that the sign of species concentration change due to advection is specified, as was discussed in the previous paragraphs. Since urban emissions are greater than advective sources for most molecules, the effects of improper choices for background concentrations are less severe than if the relative source strengths were reversed.

No specific sensitivity studies of background concentration effects have been carried out for the Bell Laboratories model, but other urban model studies (Duewer et al. (ref. 63)) have demonstrated that the effects can be important in some circumstances. It thus appears that the accurate specification of background concentrations is an important consideration if results pertaining to specific days are to be procured from modeling efforts.

Entrainment

As solar heating warms the morning air, the depth of the mixed layer increases, reaching a maximum in the mid-to-late afternoon. The air entrained into the mixed layer brings trace species with it. Two simultaneous processes occur: the increase in the volume of the mixed boundary layer tends to decrease the concentrations of the trace species, while the presence of certain species in the entrained air tends to modulate that decrease. If the entrained air contains higher concentrations of a species than the air into which entrainment occurs, a net increase in concentration may result.

Molecules present in entrained air will generally be those with reasonably long atmospheric lifetimes such as CH_4 , CO , CO_2 , H_2 , and N_2O . Of the species with intermediate lifetimes, NO_2 , O_3 , and certain of the non-methane hydrocarbons have been measured above the predawn inversion (Lea (ref. 64), Blumenthal and White (ref. 65), Siddiqi and Worley (ref. 66), and Tesche et al. (ref. 67)). It is thus required that incorporation of these species into the mixed layer be reflected in model simulations.

A number of sensitivity studies have been performed with the Bell Laboratories model to investigate the effects of entrained species. The initial conclusion (Graedel et al. (ref. 4)) was that entrainment of trace species was not

only intuitively required but produced computational results in better agreement with data than were computations performed with entrainment of pure air. More extensive work (as yet unpublished) indicates that such inclusion is critical only for species whose entrained concentrations are of the same order as, or of greater order than, concentrations in the air into which entrainment occurs. This condition appears to be often present for ozone and for the long-lifetime species mentioned previously, but not (in urban areas) for oxides of nitrogen or reactive hydrocarbons.

A parameter affecting not only the number of molecules added by entrainment but also the volume of the mixed layer is the mixed layer depth. This quantity is not always capable of being measured with precision and is seldom determined at several different times throughout a given day. A full description is required, however, for calculations attempting to simulate air quality at a specific time and place. For didactic purposes, it appears sufficient to specify mixed layer depth by joining typical morning and afternoon mixing height measurements by a theoretical curve such as those of Tennekes (ref. 68).

Emission Inventory

Emission inventories are never up to date, never complete, and of varying accuracy. Their compilation is tedious and mundane, as pointed out by Roth et al. (ref. 69), yet such work is necessary in order to derive good quantitative results from calculations. Deficiencies in the emissions inventory for a given region are generally difficult to estimate but may be the principal limitation to the accuracy of model results if other potential sources of error are carefully addressed.

Incomplete emission inventories affect calculational results differently for different species. The emission variations studies discussed in the section "Emission Variations in the Urban Environment" function also as sensitivity studies for the emission inventory. The results of those calculations showed that for the northern New Jersey urban area, the production of a variety of photochemical products was influenced markedly by changes in NO emission flux but minimally by changes in hydrocarbon emission flux. Separate studies for CO and SO₂ were not performed, but the minimal involvement of these species in urban atmospheric chemistry suggests that inaccuracies in their emission rates would not perturb the chemical system to any marked degree. The emission sources and rates for these species are also rather well defined: CO is emitted almost entirely from motor vehicles, and SO₂ largely from power generation facilities. The relative insensitivity of urban photochemistry to hydrocarbon emission fluxes is fortuitous, since hydrocarbon emissions, both anthropogenic and natural, are the least well defined of the major source terms. Nitric oxide is a product of combustion processes and its emission rates, while generally less well determined than those for CO and SO₂, will probably be more accurate than those for hydrocarbons.

To summarize, model results are reasonably sensitive to the emission rates of certain species. If the air quality on specific days is to be modeled, intensive effort will be needed to ensure a good emission inventory. Useful semi-quantitative results representing certain average conditions can generally be

derived with a less detailed picture of emissions, however, particularly if accuracy for NO emission fluxes is emphasized.

The Full Mixing Assumption

Chemical kinetic calculations require that a uniformly mixed volume at some scale size be assumed. In the urban atmosphere such an assumption is obviously inappropriate for length scales of the order of a hundred meters (the dimension of influence of a multilane highway, for example). Models generally utilize length and width scales of the order of 1 to 30 km, with the vertical dimension being equal to the mixing height (perhaps 0.3 to 2.0 km). Spatial profiles for a variety of species often show reasonable homogeneity on such scales if strong convective mixing conditions are present (Tennekes (ref. 70), Cleveland et al. (ref. 17), and Siddiqi and Worley (ref. 66)); such behavior is common on many summer days but uncommon at night.

The absence of uniform mixed conditions has been shown by Donaldson and Hilst (ref. 71) to have potentially significant effects on chemical results. It is therefore important that models be applied only to situations that can be simulated accurately by their meteorological formulation and data. This requirement currently limits the applicability of most models to days with normal mixing rather than to the inversion-stagnation periods of perhaps greatest concern from an air quality standpoint.

Summary

Potential sources of error are present in nearly every aspect of urban photochemical computations and limit the accuracy and usefulness of the results. Many of these limitations can be alleviated by suitable data-gathering efforts: solar insolation, background concentrations, entrainment considerations, and emission inventories. Difficulties with mixing and advection can be reduced by careful selection of the types of conditions to which the calculations apply. Uncertainties in the chemical formulation are the most difficult factors to assess, but it currently appears unlikely that major inaccuracies are present in the understanding of the principal processes of urban photochemistry. Those areas that seem of most concern have been the subject of sensitivity analyses or are under active investigation.

From a practical point of view, it seems unlikely that the necessary information will be available in the near future to allow urban calculations to simulate specific days and times with good accuracy. (A possible exception is the Regional Air Pollution Study for St. Louis, for which data are now being prepared for dissemination.) In the interim, it appears that model calculations can be regarded as instructive in an average semiquantitative sense and that the relative effects of selected perturbations on urban photochemistry can be assessed with a moderate degree of confidence.

DESIRABLE FIELD STUDIES

The meteorology and chemistry of the atmosphere in and near urban areas are incompletely specified, and many theoretical studies now rest on inadequate data bases. Some of the simplifications and assumptions that have been made in modeling studies have already been described. In other cases, models have not been formulated because insufficient information is available. In this section, these inadequacies are described more completely and their relative importance is assessed.

Meteorological Parameters

Perhaps the most critical need in this category is for a good specification of horizontal mixing of tropospheric air. This is particularly true for the mesoscale (20 to 200 km), although smaller scales are also imperfectly specified. Accurate statistical descriptions of mesoscale mixing are needed to determine how rapidly and completely urban air is mixed with nonurban air and thus the time scales over which the full interactive smog chemistry occurs. The variation of this mixing under differing solar insolation conditions also needs to be studied. It is knowledge in these areas that will be important in determining the fraction of precursor molecules which is converted to oxygenated products and drops out (perhaps literally) of the chemistry and the fraction which is added to the global background.

Nearly as important as horizontal mixing information is a statistical description of vertical mixing, especially under extreme meteorological conditions. Such information is crucial to determining the dilution of the urban air mass by background air. Both horizontal and vertical mixing could be studied by using relatively unreactive molecules as tracers; meteorological parameters (e.g., temperature and wind profiles) might also be appropriate.

The interplay of meteorology and chemistry is demonstrated by vertical profiles of reactive molecules. Very few measurements of this type are available; many are needed. If vertical mixing were well specified, for example, simultaneous vertical profiles of propylene and ozone would provide an indirect but reliable determination of the concentration of the hydroxyl radical, since it and ozone are the major reactants for propylene. For SO_2 , generally emitted at moderate heights from stacks, vertical diffusion both up and down is of interest, as is conversion in transit to sulfate species. Additional examples of the uses of height profiles of reactive compounds abound.

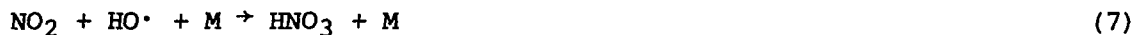
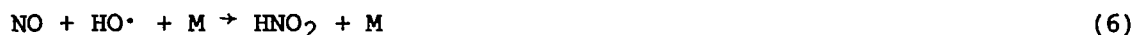
Chemical Parameters

From the standpoint of the chemist, the history of chemical species measurements in the troposphere has been one of emphasis on precursors rather than on products. An obvious reason for this preference is that precursors are generally easier to measure and their concentrations are higher. The products, however, are often the more toxic. The product source and sink mechanisms for many systems are poorly specified but are important considerations in assessing the global atmospheric cycles of chemical elements. The measurement of a wide vari-

ety of precursor-product pairs is thus to be encouraged, as is the measurement of the free radicals that so often control the transition from precursor to product.

The only free-radical intermediate thus far measured in the troposphere is $\text{HO}\cdot$. The limited number of measurements suggests a typical diurnal ground-level peak of the order of $2\text{--}3 \times 10^6$ molecules- cm^{-3} (Wang et al. (ref. 72), Davis et al. (ref. 34), and Perner et al. (ref. 73)); the variations of the hydroxyl concentrations with such factors as latitude, time of year, amount of cloud cover, time of day, and concentrations of other atmospheric species remain to be determined. Other atmospherically important radicals that have not been detected in situ but have been measured under laboratory conditions are $\text{HO}_2\cdot$ (Radford et al. (ref. 74) and Becker et al. (ref. 75)), $\text{CH}_3\text{O}_2\cdot$ (Parkes et al. (ref. 76)), and $\text{NO}_3\cdot$ (Graham and Johnston (ref. 77)). The estimated atmospheric diurnal peak concentrations of these radicals in urban atmospheres (as predicted by the Bell Laboratories kinetic photochemical model) are given in table II.

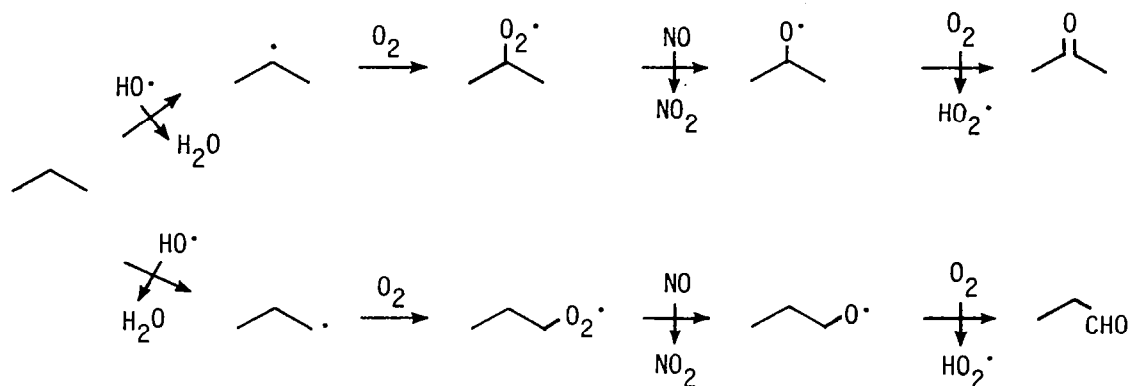
Several precursor-product pairs involving odd nitrogen compounds are of atmospheric interest. All involve the formation of acids. The production reactions are



Of these compounds, NO and NO_2 are readily measured and HNO_3 is measurable with some difficulty. HNO_2 has been detected only once in the atmosphere (Nash (ref. 13)). Pernitric acid (HO_2NO_2) has not been measured in ambient air but has been detected in the laboratory (Niki et al. (ref. 54)). Approximate urban atmospheric concentrations for these compounds, based on a combination of data and model studies, are given in table III. The most chemically instructive measurements would be simultaneous determinations of the concentrations of both members of a precursor-product pair. Determinations at different times of day and under different meteorological conditions are desirable. The concurrent measurement of the concentration of the linking species would be of great value.

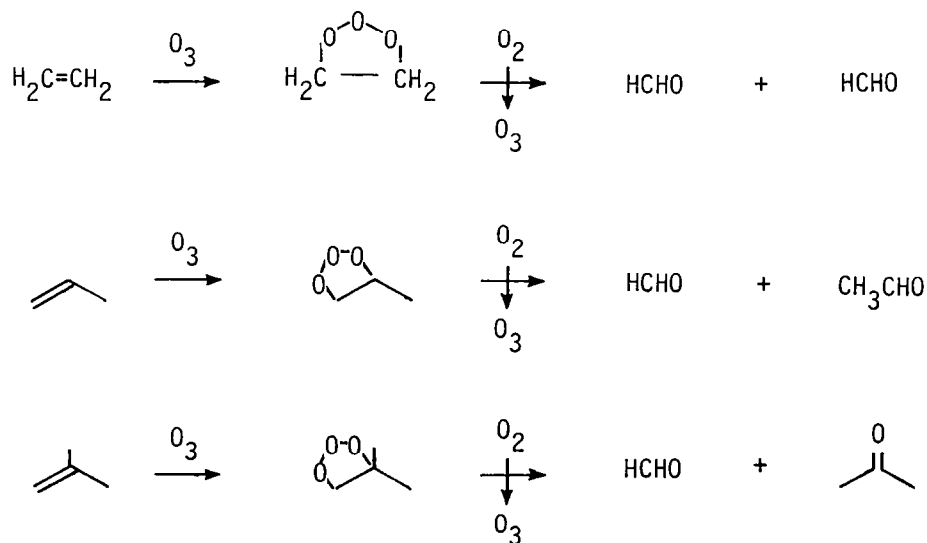
Measurements of individual organic compounds in the atmosphere are sparse, despite the knowledge that such compounds play important roles in atmospheric chemical processes. The situation is compounded by the diversity of compounds and by the tendency for the same product to result from several precursors and by several chemical paths. Most common organic emittants are hydrocarbon compounds, however, and their oxidation products are aldehydes, ketones, alcohols,

and acids. The chain-initiating reaction is usually with the hydroxyl radical, although sometimes with ozone. A sample sequence is the twin-route reaction of propane with hydroxyl:

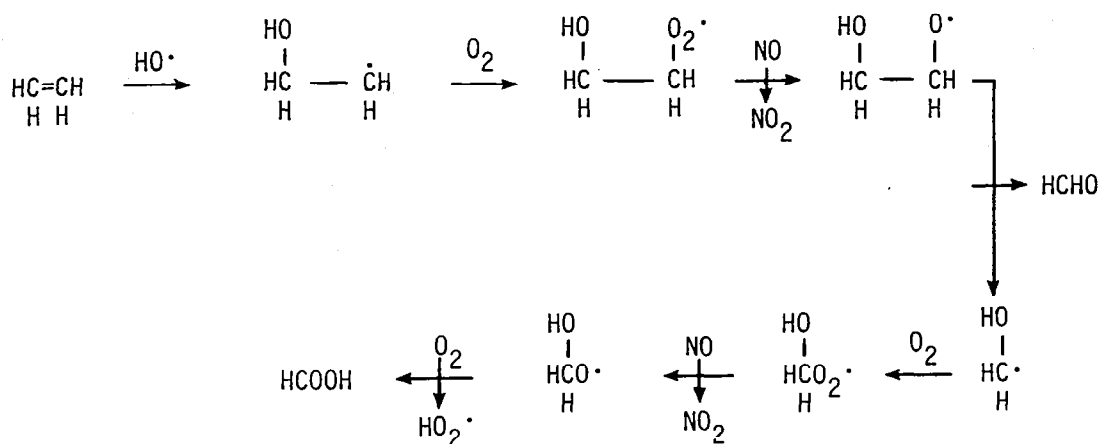


(The short orthogonal arrows indicate the progression of the attacking molecule from reactant to product.) In this sequence, the product is acetone or propanal, depending on the hydrogen abstraction site. Both products are subject to photodissociation at tropospheric wavelengths, and both have sources other than this sequence.

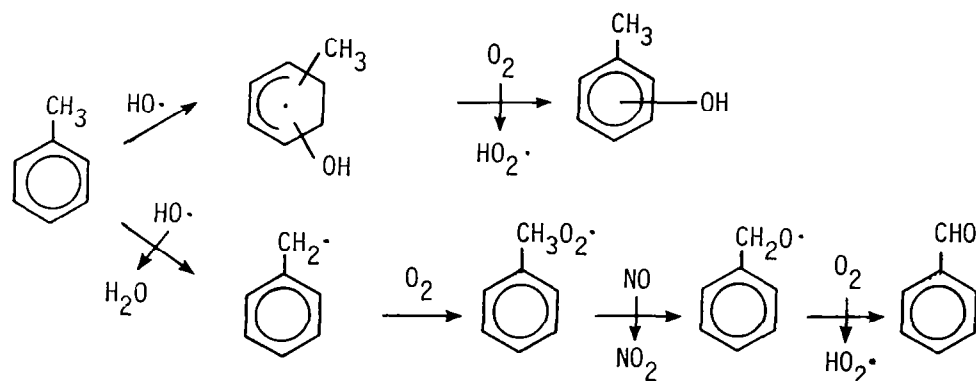
More diverse chemistry results with the alkenes. The reaction of ozone with 1-alkenes produces formaldehyde (HCHO), a second carbonyl product, and perhaps other oxygenated species (Herron and Huie (ref. 78)):



Many of the same products result from hydroxyl attack on alkenes. Such reactions are capable of forming acids as well as carbonyl compounds, as demonstrated for ethene, as follows:



The atmospheric fates of aromatic compounds have received little attention, but the most plausible sequences appear to involve hydroxyl initiation. For toluene, these include:



Because of the multiplicity of these chains, precursor-product pairs are defined less precisely than is the case with the odd nitrogen compounds. For some products, however, the principal precursor or precursors can be deduced from information concerning relative concentrations of possible precursors and their rate constants for hydroxyl radical or ozone reaction. A selected list of precursors and products developed by this technique is given in table IV. As with the odd nitrogen compounds of table III, concurrent measurement of precursor-product pairs, and if possible of the linking species, is most useful, as are measurements for a variety of temporal and meteorological conditions.

CONCLUDING REMARKS

The ability to model satisfactorily the processes of urban atmospheres is presently restricted to selected chemical processes, a handful of geographical regions, and stringently stratified meteorological conditions. Nonetheless, much has been learned. Such distinct situations as urban workdays, urban Sundays, transport and chemistry upwind of, within, and downwind of urban areas, and overwater transport have been qualitatively simulated by computer techniques. The agreement with ambient data appears to be reasonably good, sug-

gesting that at least the principal processes of urban photochemistry and meteorology are fairly well understood.

Simulations of urban photochemistry with altered source conditions have also been completed. Although the generality of the results remains to be established, the results suggest that, at least in northern New Jersey, nitric oxide is the rate-limiting reactant for many of the principal photochemical smog processes. Decreases in its emission flux thus appear likely to result in decreases in the concentrations of a variety of photochemical products, both within the urban area and downwind of it.

Many of the details of atmospheric chemical processes are poorly determined. To this end, concurrent measurements of a variety of precursors, linking species, and products are desirable. Suggestions for and chemical justification of such groups have been given. The availability of such data will markedly enhance understanding of the chemistry of the urban atmosphere.

REFERENCES

1. Subcommittee on Ozone and Other Photochemical Oxidants: Ozone and Other Photochemical Oxidants - Volume I, EPA-600/1-76-027a, U.S. Environ. Prot. Agency, Aug. 1976, pp. 45-125. (Available from NTIS as PB-260 570.)
2. Demerjian, Kenneth L.; Kerr, J. Alistair; and Calvert, Jack G.: The Mechanism of Photochemical Smog Formation. Advances in Environmental Science and Technology, Volume 4, James N. Pitts, Jr., and Robert L. Metcalf, eds., John Wiley & Sons, c.1974, pp. 1-262.
3. Panel on Vapor-Phase Organic Pollutants: Vapor-Phase Organic Pollutants Volatile Hydrocarbons and Oxidation Products. EPA-600/1-75-005, U.S. Environ. Prot. Agency, Oct. 1975. (Available from NTIS as PB-249 357.)
4. Graedel, T. E.; Farrow, L. A.; and Weber, T. A.: Kinetic Studies of the Photochemistry of the Urban Troposphere. Atmos. Environ., vol. 10, no. 12, 1976, pp. 1095-1116.
5. Heicklen, Julian: Atmospheric Chemistry. Academic Press, Inc., 1976.
6. Winkler, Peter: The Growth of Atmospheric Aerosol Particles as a Function of the Relative Humidity - II. An Improved Concept of Mixed Nuclei. J. Aerosol Sci., vol. 4, no. 5, Sept. 1973, pp. 373-387.
7. Graedel, T. E.; Farrow, L. A.; and Weber, T. A.: The Influence of Aerosols on the Chemistry of the Troposphere. Chemical Kinetics Data for the Upper and Lower Atmosphere, Int. J. Chem. Kinet., Symp. No. 1, 1975, pp. 581-594.
8. Warneck, Peter: Role of Hydroxyl and Hydroperoxyl Radical in the Troposphere. Tellus, vol. 26, nos. 1-2, 1974, pp. 39-46.
9. Air Quality Criteria for Photochemical Oxidants. NAPCA Publ. No. AP-63, U.S. Environ. Prot. Agency, [1970].
10. Cleveland, William S.; Kleiner, Beat; and Warner, Jack L.: Robust Statistical Methods and Photochemical Air Pollution Data. J. Air Pollut. Control Assoc., vol. 26, no. 1, Jan. 1976, pp. 36-38.
11. Altshuller, A. P.; and McPherson, S. P.: Spectrophotometric Analysis of Aldehydes in the Los Angeles Atmosphere. J. Air Pollut. Control Assoc., vol. 13, no. 3, 1963, pp. 109-111.
12. Gay, Bruce W., Jr.; and Bufalini, Joseph J.: Hydrogen Peroxide in the Urban Atmosphere. Adv. Chem. Ser. No. 113, 1972, pp. 255-263.
13. Nash, T.: Nitrous Acid in the Atmosphere and Laboratory Experiments on Its Photolysis. Tellus, vol. 26, nos. 1-2, 1974, pp. 175-179.
14. Spicer, Chester W.: Nonregulated Photochemical Pollutants Derived From Nitrogen Oxides. Scientific Seminar on Automotive Pollutants, EPA-600/9-75-003, U.S. Environ. Prot. Agency, Feb. 1975.

15. Graedel, T. E.: Sulfur Dioxide, Sulfate Aerosol, and Urban Ozone. *Geophys. Res. Lett.*, vol. 3, no. 3, Mar. 1976, pp. 181-184.
16. Bruntz, S. M.; Cleveland, W. S.; Graedel, T. E.; Kleiner, B.; and Warner, J. L.: Ozone Concentrations in New Jersey and New York: Statistical Association With Related Variables. *Science*, vol. 186, no. 4160, Oct. 18, 1974, pp. 257-259.
17. Cleveland, W. S.; Graedel, T. E.; Kleiner, B.; and Warner, J. L.: Sunday and Workday Variations in Photochemical Air Pollutants in New Jersey and New York. *Science*, vol. 186, no. 4168, Dec. 13, 1974, pp. 1037-1038.
18. Farrow, L. A.; Graedel, T. E.; and Weber, T. A.: Heterogeneous Removal of Free Radicals by Aerosols in the Urban Troposphere. *ACS Symp. Ser.*, vol. 17, 1975, pp. 17-27.
19. Graedel, T. E.: Functional Group Analysis of Large Chemical Kinetic Systems. *J. Phys. Chem.*, vol. 81, no. 25, 1977, pp. 2372-2374.
20. Graedel, Thomas E.; Farrow, Leonilda A.; and Weber, Thomas A.: Photochemistry of the "Sunday Effect." *Environ. Sci. & Technol.*, vol. 11, no. 7, July 1977, pp. 690-694.
21. Altshuller, A. P.: Evaluation of Oxidant Results at CAMP Sites in the United States. *J. Air Pollut. Control Assoc.*, vol. 25, no. 1, Jan. 1975, pp. 19-24.
22. Cleveland, W. S.; Kleiner, B.; McRae, J. E.; and Warner, J. L.: Photochemical Air Pollution: Transport From the New York City Area Into Connecticut and Massachusetts. *Science*, vol. 191, no. 4223, Jan. 16, 1976, pp. 179-181.
23. Bruckman, Leonard: Suspended Particulate Transport in Connecticut: An Investigation Into the Relationship Between TSP Concentrations and Wind Direction in Connecticut. *Connecticut Dep. Environ. Prot.*, Dec. 24, 1976.
24. Cunningham, Paul T.; Johnson, Stanley A.; and Yang, Ralph T.: Variations in Chemistry of Airborne Particulate Material With Particle Size and Time. *Environ. Sci. & Technol.*, vol. 8, no. 2, 1974, pp. 131-135.
25. Grosjean, Daniel; and Friedlander, Sheldon K.: Gas-Particle Distribution Factors for Organic and Other Pollutants in the Los Angeles Atmosphere. *J. Air Pollut. Control Assoc.*, vol. 25, no. 10, Oct. 1975, pp. 1038-1044.
26. Liroy, Paul J.; Wolff, George T.; Czachor, Joseph S.; Coffey, Peter E.; Stasiuk, William N.; and Romano, David: Evidence of High Atmosphere Concentrations of Sulfates Detected at Rural Sites in the Northeast. *J. Environ. Sci. & Health*, vol. A12, nos. 1 & 2, 1977, pp. 1-14.
27. Spicer, C. W.: Formation and Transport of Ozone in the Troposphere. *Proceedings of Specialty Conference on Ozone/Oxidants - Interaction With the Total Environment*, *Air Pollut. Control Assoc.*, 1976, pp. 207-220.

28. Graedel, T. E.; Farrow, L. A.; and Weber, T. A.: Urban Kinetic Chemical Calculations With Altered Source Conditions. *Atmos. Environ.*, vol. 12, 1978.
29. Graedel, T. E.; Farrow, L. A.: Kinetic Photochemistry Downwind Over Water From Urban Areas. *J. Geophys. Res.*, vol. 82, no. 31, Oct. 20, 1977, pp. 4943-4946.
30. Dimitriadis, B.: The Role of NO_x in the Ambient NO_2 and Oxidant Problems. Smog Chamber Studies. Scientific Seminar on Automotive Pollutants, EPA-600/9-75-003, U.S. Environ. Prot. Agency, Feb. 1975.
31. Hecht, Thomas A.: Smog Simulation Models and Their Use in Evaluating Air Quality Control Strategies. Scientific Seminar on Automotive Pollutants, EPA-600/9-75-003, U.S. Environ. Prot. Agency, Feb. 1975.
32. Appendix 9-3. Photochemical Rates, Hydrocarbon Reactivities, Validation With Data, and Sensitivity Studies. Development of an Air Pollution Model for the San Francisco Bay Area - Final Report to the National Science Foundation. Volume 2, M. C. MacCracken and G. D. Sauter, eds., UCRL-51920 Vol. 2, Lawrence Livermore Lab., Oct. 1, 1975.
33. Stedman, D. H.; and Jackson, J. O.: The Photostationary State in Photochemical Smog. Chemical Kinetics Data for the Upper and Lower Atmosphere, *Int. J. Chem. Kinet.*, Symp. No. 1, 1975, pp. 493-501.
34. Davis, D. D.; Heaps, W.; and McGee, T.: Direct Measurements of Natural Tropospheric Levels of OH Via an Aircraft Borne Tunable Dye Laser. *Geophys. Res. Lett.*, vol. 3, no. 6, June 1976, pp. 331-333.
35. Farrow, L. A.; and Graedel, T. E.: Steady State Approximations and Urban Atmospheric Chemistry. *J. Phys. Chem.*, vol. 81, no. 25, 1977, pp. 2480-2483.
36. Gorse, R. A.; and Volman, D. H.: Photochemistry of the Gaseous Hydrogen Peroxide-Carbon Monoxide System. II. Rate Constants for Hydroxyl Radical Reactions With Hydrocarbons and for Hydrogen Atom Reactions With Hydrogen Peroxide. *J. Photochem.*, vol. 3, nos. 2-3, 1974, pp. 115-122.
37. Hansen, D. A.; Atkinson, R.; and Pitts, J. N., Jr.: Rate Constants for the Reaction of OH Radicals With a Series of Aromatic Hydrocarbons. *J. Phys. Chem.*, vol. 79, no. 17, Aug. 14, 1975, pp. 1763-1766.
38. Cukier, R. I.; Levine, H. B.; and Shuler, K. E.: Nonlinear Sensitivity Analysis of Multiparameter Model Systems. *J. Phys. Chem.*, vol. 81, no. 25, 1977, pp. 2365-2366.
39. Duewer, William H.; Wuebbles, Donald J.; Ellsaesser, Hugh W.; and Chang, Julius S.: NO_x Catalytic Ozone Destruction: Sensitivity to Rate Coefficients. *J. Geophys. Res.*, vol. 82, no. 6, Feb. 20, 1977, pp. 935-942.

40. Altshuller, Aubrey P.; Lonneman, William A.; Sutterfield, Frank D.; and Kopczynski, Stanley L.: Hydrocarbon Composition of the Atmosphere of the Los Angeles Basin - 1967. *Environ. Sci. & Technol.*, vol. 5, no. 10, 1971, pp. 1009-1016.
41. Grob, K.; and Grob, G.: Gas-Liquid Chromatographic-Mass Spectrometric Investigation of C₆-C₂₀ Organic Compounds in an Urban Atmosphere. *J. Chromatog.*, vol. 62, no. 1, Oct. 18, 1971, pp. 1-13.
42. Leighton, Philip A.: Photochemistry of Air Pollution. Academic Press, Inc., 1961.
43. Morris, E. D., Jr.; and Niki, H.: Reaction of the Nitrate Radical With Acetaldehyde and Propylene. *J. Phys. Chem.*, vol. 78, no. 13, June 20, 1974, pp. 1337-1338.
44. Davis, D. D.; and Klauber, Gary: Atmospheric Gas Phase Oxidation Mechanisms for the Molecule SO₂. Chemical Kinetics Data for the Upper and Lower Atmosphere, *Int. J. Chem. Kinet.*, Symp. No. 1, 1975, pp. 543-556.
45. Graedel, T. E.: The Homogeneous Chemistry of Atmospheric Sulfur. *Rev. Geophys. & Space Phys.*, vol. 15, no. 4, Nov. 1977, pp. 421-428.
46. Crutzen, Paul J.: Gas-Phase Nitrogen and Methane Chemistry in the Atmosphere. Physics and Chemistry of Upper Atmospheres, B. M. McCormac, ed., D. Reidel Publishing Co., c.1973, pp. 110-124.
47. Graedel, T. E.: The Oxidation of Ammonia, Hydrogen Sulfide, and Methane in Nonurban Tropospheres. *J. Geophys. Res.*, vol. 82, no. 37, Dec. 20, 1977, pp. 5917-5922.
48. Charlson, R. J.; Porch, W. M.; Waggoner, A. P.; and Ahlquist, N. C.: Background Aerosol Light Scattering Characteristics: Nephelometric Observations at Mauna Loa Observatory Compared With Results at Other Locations. *Tellus*, vol. 26, no. 3, 1974, pp. 345-360.
49. Glasson, William A.; and Heuss, Jon M.: Synthesis and Evaluation of Potential Atmospheric Eye Irritants. *Environ. Sci. & Technol.*, vol. 11, no. 4, Apr. 1977, pp. 395-398.
50. Calvert, Jack G.: Interactions of Air Pollutants. Proceedings of the Conference on Health Effects of Air Pollutants, Natl. Acad. Sci., 1973, pp. 19-101.
51. Hampson, Robert F., Jr.; and Garvin, David, eds.: Chemical Kinetic and Photochemical Data for Modelling Atmosphere Chemistry. NBS Tech. Note 866, U.S. Dep. Commer., June 1975.
52. Howard, C. J.; and Evenson, K. M.: Laser Magnetic Resonance Study of HO₂ Chemistry. *EOS Trans., American Geophys. Union*, vol. 58, no. 6, June 1977, p. 464.

53. Levine, Stuart Z.; Uselman, William M.; Chan, Walter H.; Calvert, Jack G.; and Shaw, John H.: The Kinetics and Mechanism of the $\text{HO}_2\text{-NO}_2$ Reactions; the Significance of Peroxynitric Acid Formation in Photochemical Smog. *Chem. Phys. Lett.*, vol. 48, no. 3, June 15, 1977, pp. 528-535.
54. Niki, H.; Maker, P. D.; Savage, C. M.; and Breitenbach, L. P.: Fourier Transform IR Spectroscopic Observation of Pernitric Acid Formed Via $\text{HOO} + \text{NO}_2 \rightarrow \text{HOONO}_2$. *Chem. Phys. Lett.*, vol. 45, no. 3, Feb. 1, 1977, pp. 564-566.
55. Calvert, Jack G.; Kerr, J. Alistair; Demerjian, Kenneth L.; and McQuigg, Robert D.: Photolysis of Formaldehyde as a Hydrogen Atom Source in the Lower Atmosphere. *Science*, vol. 175, no. 4023, Feb. 18, 1972, pp. 751-752.
56. Houston, Paul L.; and Moore, C. Bradley: Formaldehyde Photochemistry: Appearance Rate, Vibrational Relaxation, and Energy Distribution of the CO Product. *J. Chem. Phys.*, vol. 65, no. 2, July 15, 1976, pp. 757-770.
57. Lewis, Roger S.; Tang, Kenneth Y.; and Lee, Edward K. C.: Photoexcited Chemiluminescence Spectroscopy: Detection of Hydrogen Atoms Produced From Single Vibronic Level Photolysis of Formaldehyde (A^1A_2). *J. Chem. Phys.*, vol. 65, no. 7, Oct. 1, 1976, pp. 2910-2911.
58. Osif, T. L.; and Heicklen, Julian: Oxidation of HCO Radicals. *J. Phys. Chem.*, vol. 80, no. 14, July 1976, pp. 1526-1531.
59. Niki, H.; Maker, P.; Savage, C.; and Breitenbach, L.: IR Fourier-Transform Spectroscopic Studies of Atmospheric Reactions. The 12th Informal Conference on Photochemistry - Extended Abstracts, Natl. Bur. Stand., U.S. Dep. Commer., June-July 1976, pp. N2-1 - N2-4.
60. Marchgraber, Reinhold M.: Development of Standard Instruments for Radiation Measurements. *Meteorol. Monogr.*, vol. 11, no. 33, Oct. 1970, pp. 302-314.
61. Graedel, T. E.; Farrow, L. A.; and Weber, T. A.: The Effects of Variations in Bulk Meteorological Parameters on Ozone Concentrations. Symposium on Atmospheric Diffusion and Air Pollution - Preprints, American Meteorol. Soc., Sept. 1974, p. 115.
62. Peterson, J. T.; and Demerjian, K. L.: The Sensitivity of Computed Ozone Concentrations to U.V. Radiation in the Los Angeles Area. *Atmos. Environ.*, vol. 10, no. 6, 1976, pp. 459-468.
63. Duewer, W. H.; MacCracken, M. C.; and Walton, J. J.: The Livermore Regional Air Quality Model: II. Verification and Sample Application in the San Francisco Bay Area. Preprint UCRL-77475 Pt. 2, Lawrence Livermore Lab., Dec. 18, 1975.
64. Lea, Duane A.: Vertical Ozone Distribution in the Lower Troposphere Near an Urban Pollution Complex. *J. Appl. Meteorol.*, vol. 7, no. 2, Apr. 1968, pp. 252-267.

65. Blumenthal, D. L.; and White, W. H.: The Stability and Long Range Transport of Ozone or Ozone Precursors. Paper presented at the 68th Annual Meeting of the Air Pollution Control Association (Boston, Massachusetts), June 1975.
66. Siddiqi, Aziz A.; and Worley, Frank L., Jr.: Urban and Industrial Air Pollution in Houston, Texas - I. Hydrocarbons. *Atmos. Environ.*, vol. 11, no. 2, 1977, pp. 131-143.
67. Tesche, T. W.; Ogren, J. A.; and Blumenthal, D. L.: Ozone Concentrations in Power Plant Plumes: Comparison of Models and Sampling Data. International Conference on Photochemical Oxidant Pollution and Its Control - Proceedings: Volume I, EPA-600/3-77-001a, U.S. Environ. Prot. Agency, Jan. 1977, pp. 157-171. (Available from NTIS as PB-264 232.)
68. Tennekes, H.: A Model for the Dynamics of the Inversion Above a Convective Boundary Layer. *J. Atmos. Sci.*, vol. 30, no. 4, May 1973, pp. 558-567.
69. Roth, Philip M.; Roberts, Philip J. W.; Liu, Mei-Kao; Reynolds, Steven D.; and Seinfeld, John H.: Mathematical Modeling of Photochemical Air Pollution - II. A Model and Inventory of Pollutant Emissions. *Atmos. Environ.*, vol. 8, no. 1, Jan. 1974, pp. 97-130.
70. Tennekes, Hendrik: The Atmospheric Boundary Layer. *Phys. Today*, vol. 27, no. 1, Jan. 1974, pp. 52-63.
71. Donaldson, Coleman duP.; and Hilst, Glenn R.: Effect of Inhomogeneous Mixing on Atmospheric Photochemical Reactions. *Environ. Sci. & Technol.*, vol. 6, no. 9, Sept. 1972, pp. 812-821.
72. Wang, Charles C.; Davis, L. I., Jr.; Wu, C. H.; Japar, S.; Niki, H.; and Weinstock, B.: Hydroxyl Radical Concentrations Measured in Ambient Air. *Science*, vol. 189, no. 4205, Sept. 5, 1975, pp. 797-800.
73. Perner, D.; Ehhalt, D. H.; Pätz, H. W.; Platt, U.; Röth, E. P.; and Volz, A.: OH-Radicals in the Lower Troposphere. *Geophys. Res. Lett.*, vol. 3, no. 8, Aug. 1976, pp. 466-468.
74. Radford, H. E.; Evenson, K. M.; and Howard, Carleton J.: HO₂ Detected by Laser Magnetic Resonance. *J. Chem. Phys.*, vol. 60, no. 8, Apr. 15, 1974, pp. 3178-3183.
75. Becker, K. H.; Fink, E. H.; Langen, P.; and Schurath, U.: Near Infrared Emission Bands of the HO₂ Radical. *J. Chem. Phys.*, vol. 60, no. 11, June 1, 1974, pp. 4623-4625.
76. Parkes, D. A.; Paul, D. M.; Quinn, C. P.; and Robson, R. C.: The Ultraviolet Absorption by Alkylperoxy Radicals and Their Mutual Reactions. *Chem. Phys. Lett.*, vol. 23, no. 3, Dec. 1, 1973, pp. 425-429.

77. Graham, Richard A.; and Johnston, Harold S.: The Photochemistry of NO_3 and the Kinetics of the $\text{N}_2\text{O}_5\text{-O}_3$ System. J. Phys. Chem., vol. 82, no. 3, Feb. 1978, pp. 254-268.
78. Herron, John T.; and Huie, Robert E.: Stopped-Flow Studies of the Mechanisms of Ozone-Alkene Reactions in the Gas Phase. Ethylene. J. American Chem. Soc., vol. 99, no. 16, Aug. 3, 1977, pp. 5430-5435.

TABLE I.- PEAK CONCENTRATIONS FOR MINOR ATMOSPHERIC COMPOUNDS

Compound	Computed peak concentration, ppm	Observed peak concentration, ppm	Location	Reference
$\text{CH}_2=\text{CHCHO}$	1.3×10^{-2}	1.4×10^{-2}	Los Angeles, Calif.	Altshuller and McPherson (ref. 11)
CH_3CHO	7.7×10^{-3}	1.2×10^{-2}	Bayonne, N.J.	(a)
$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$	2.9×10^{-3}	3.7×10^{-3}	Hoboken, N.J.	Lonneman (Private communication, 1974)
HCHO	6.5×10^{-3}	8×10^{-3}	Bayonne, N.J.	Cleveland and Kleiner (Private communication, 1974)
H_2O_2	6.1×10^{-2}	4×10^{-2}	Hoboken, N.J.	Gay and Bufalini (ref. 12)
HNO_2	3.4×10^{-4}	3.2×10^{-3}	South England	Nash (ref. 13)
HNO_3	3.9×10^{-3}	6×10^{-3}	St. Louis, Mo.	Spicer (ref. 14)

^aThe observed Bayonne concentration of CH_3CHO is based on the Bayonne observation of HCHO and the assumptions that the total aldehyde/formaldehyde ratio of Altshuller and McPherson (ref. 11) holds in northern New Jersey and that the total aldehydes concentration minus the formaldehyde concentration is essentially equal to the CH_3CHO concentration.








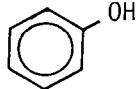

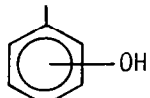

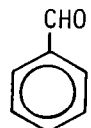
TABLE II.- MEASUREMENT NEEDS: FREE RADICALS

Species	Approximate concentration, molecules-cm ⁻³
HO•	1×10^6
HO ₂ •	6×10^8
NO ₃ •	5×10^8
CH ₃ O ₂ •	1×10^8

TABLE III.- MEASUREMENT NEEDS: ODD NITROGEN PRECURSORS AND PRODUCTS

Precursor	Approximate concentration, ppb	Linking species	Product	Approximate concentration, ppb
NO	10	HO•	HNO ₂	0.4
NO ₂	15	HO•	HNO ₃	4
NO ₂	15	HO ₂ •	HO ₂ NO ₂	?

TABLE IV.- MEASUREMENT NEEDS: ORGANIC PRECURSORS AND PRODUCTS

Precursor	Approximate concentration, ppb	Linking species	Product	Approximate concentration, ppb
$\text{H}_2\text{C}=\text{CH}_2$ 	20 10	$\text{O}_3, \text{HO}\cdot$	$^a\text{HCHO}$	10
	5			
$\text{H}_2\text{C}=\text{CH}_2$ 	20 10	$\text{HO}\cdot$	HCOOH	10
	5			
	5	O_3		3
	25	$\text{HO}\cdot$		?
	50	$\text{HO}\cdot$		?
	50	$\text{HO}\cdot$		?

^aAlso directly emitted by sources.

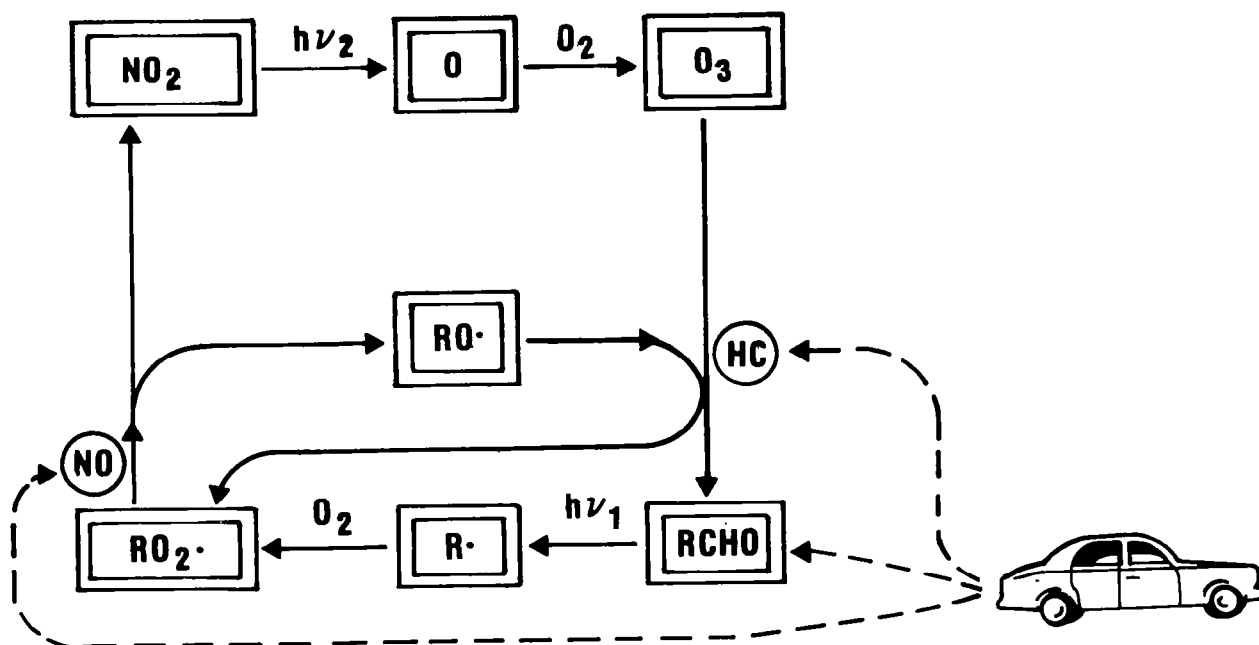


Figure 1.- Initiation and propagation of free-radical chemical chains in urban atmosphere. Sequence is initiated by photodissociation of aldehyde molecule, followed by oxidation of NO and hydrocarbon (HC) emittants.

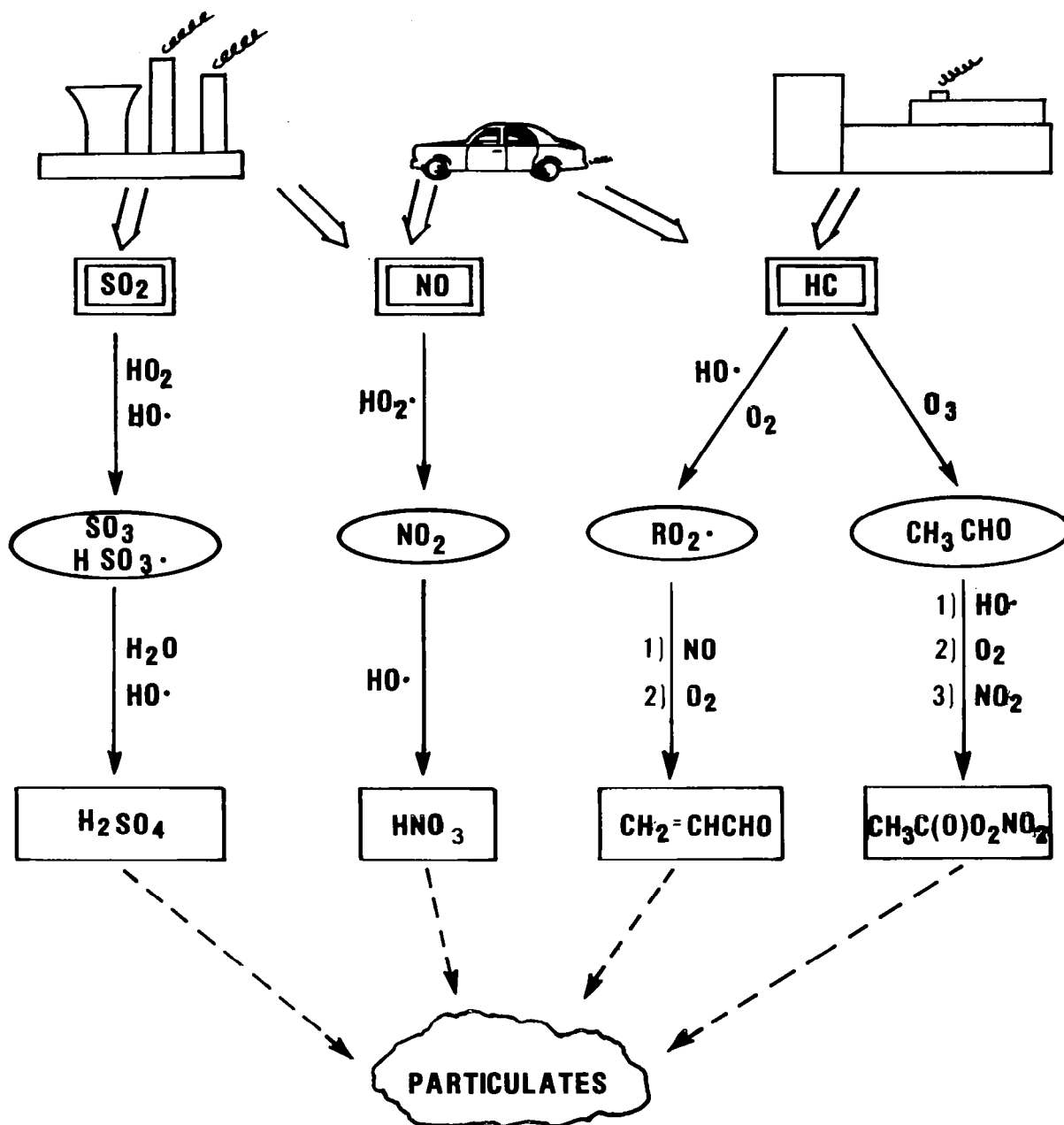


Figure 2.- Reaction sequences for formation of oxidized chemical products from urban precursors.

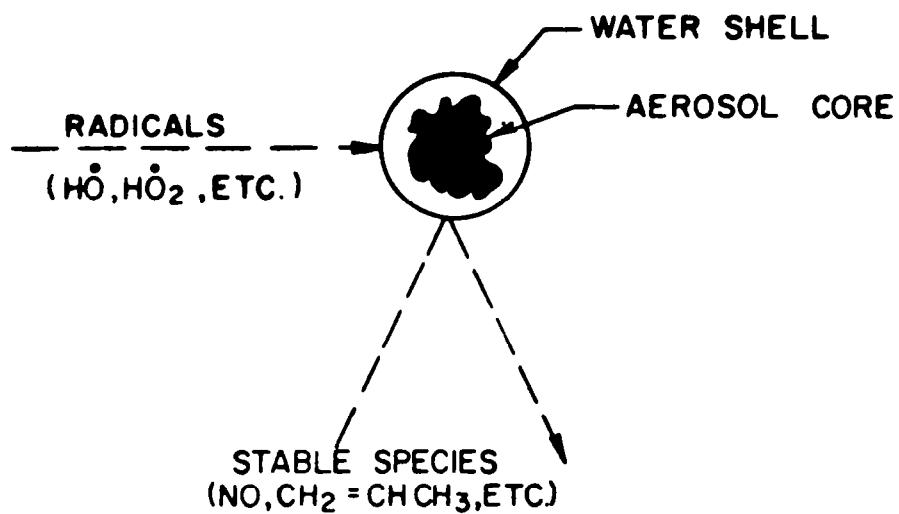


Figure 3.- Schematic representation of water-shell aerosol model for impact removal of radicals.

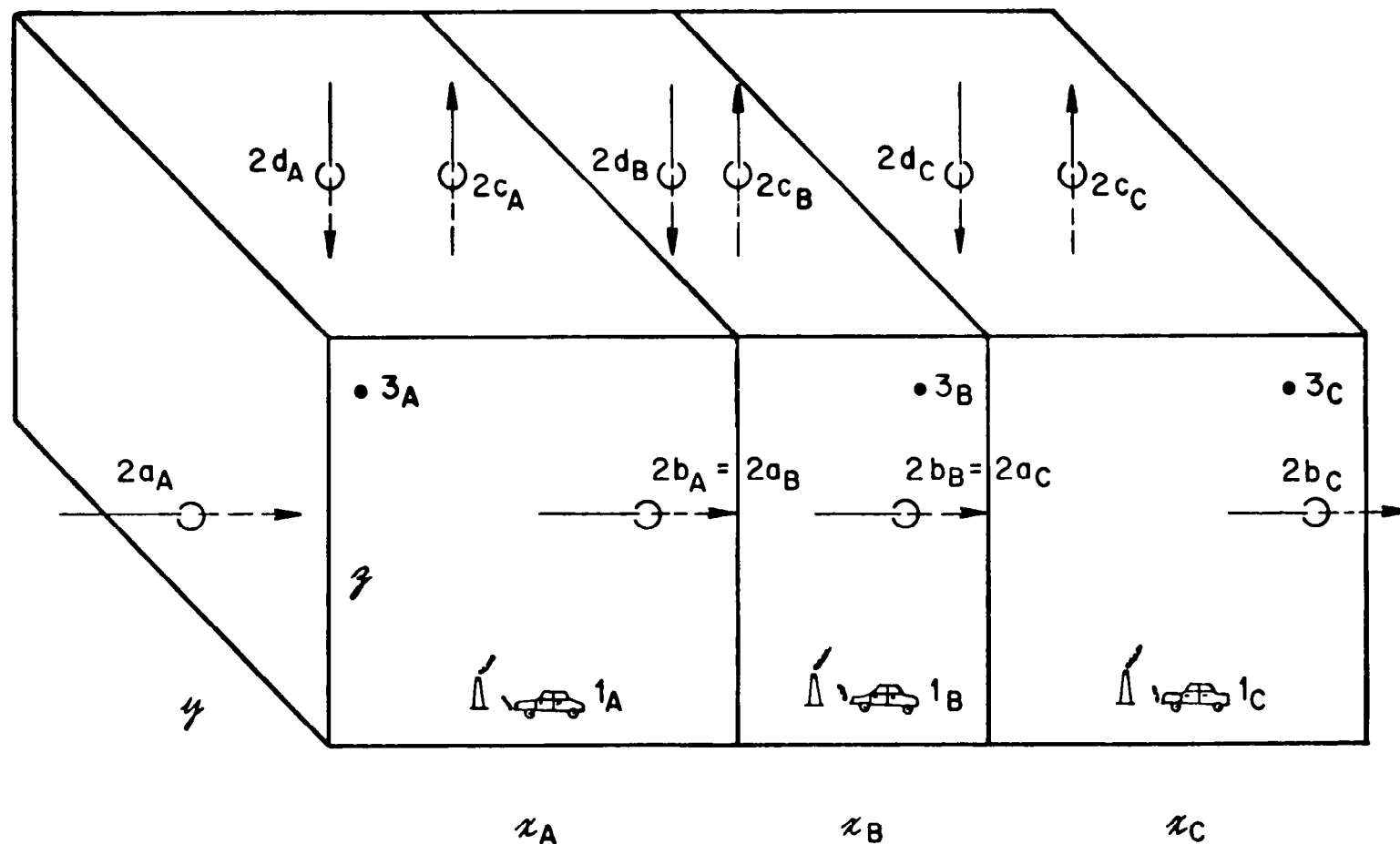


Figure 4.- Schematic representation of 3 x 1 reactant volume sequence. Symbols 1 refer to concentration changes resulting from source injection, symbols 2 to concentration changes resulting from meteorological processes, and symbols 3 to concentration changes resulting from chemical processes.

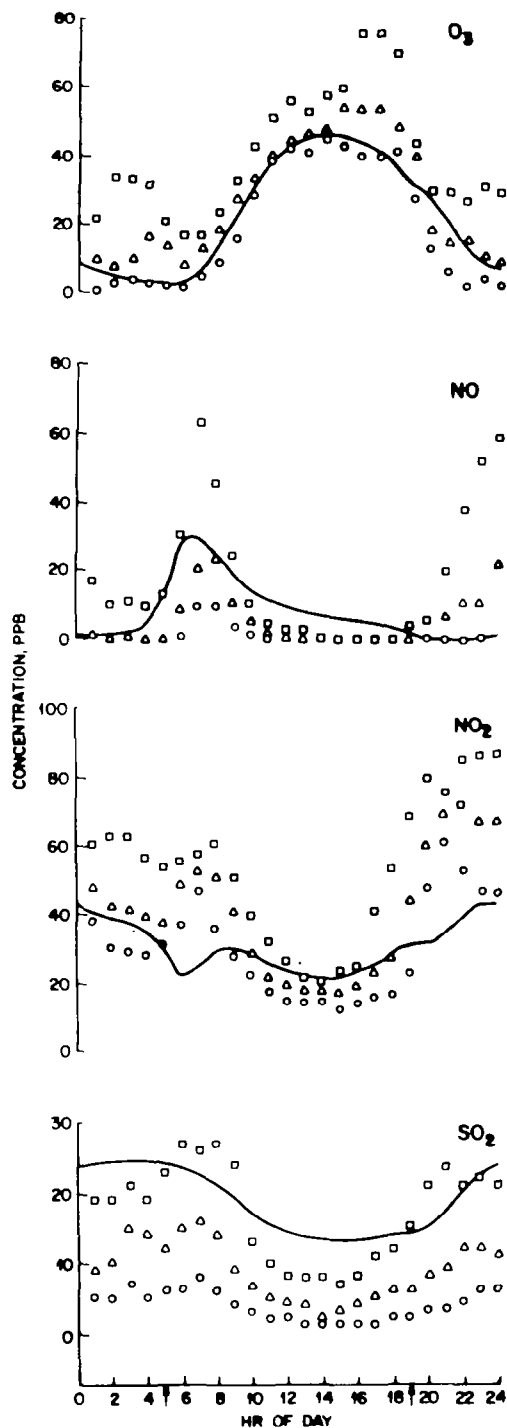


Figure 5.- Computed diurnal concentration patterns (solid lines) for Hudson County, N.J., compared with measured concentration distribution parameters: squares indicate upper quartile; triangles, median; and circles, lower quartile. Arrows on abscissa indicate times of sunrise and sunset.

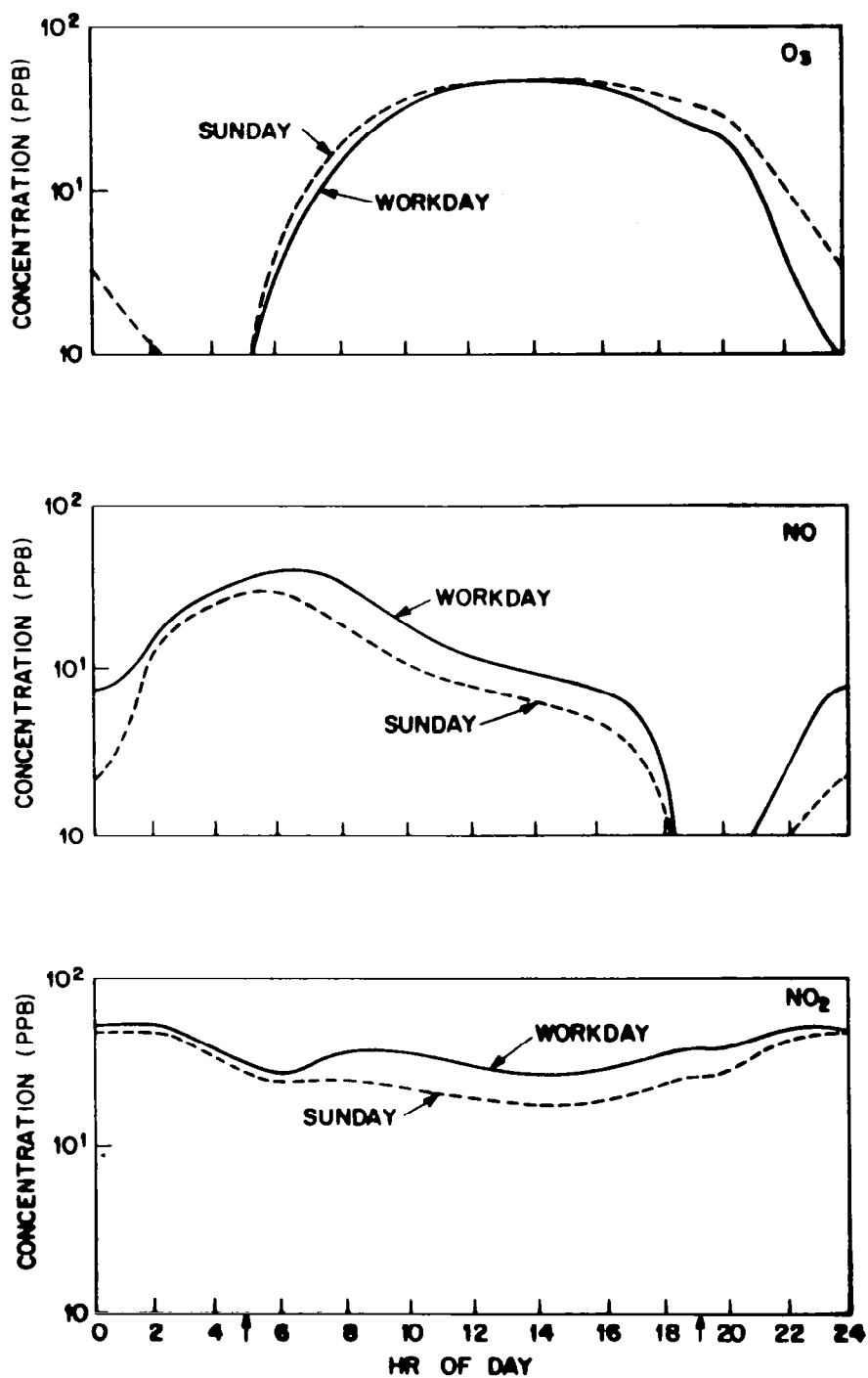


Figure 6.- Computed diurnal concentration patterns for workdays and Sundays in Hudson County, N.J. Arrows on abscissa indicate times of sunrise and sunset.

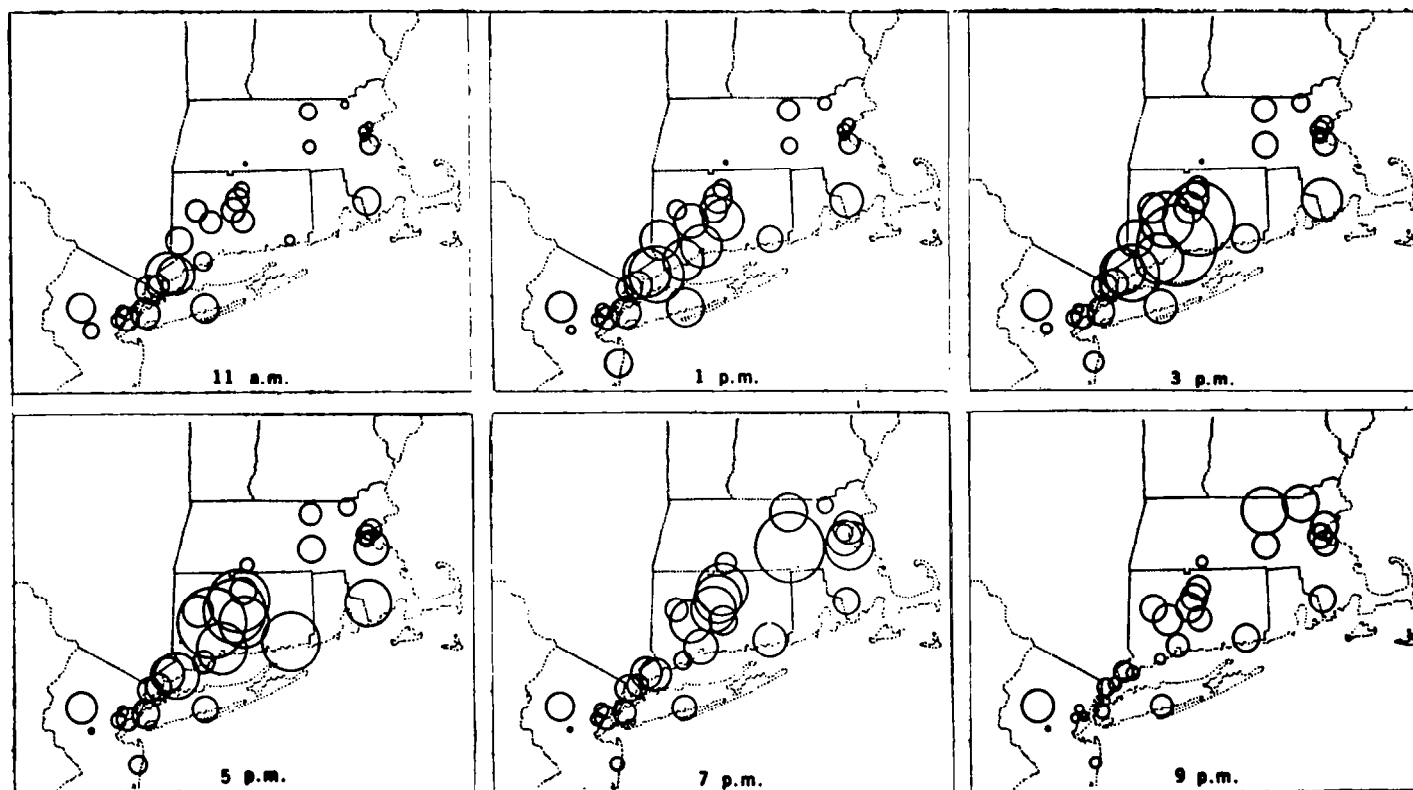


Figure 7.- Ozone concentrations at air monitoring sites in Northeastern United States measured at six different times during July 2, 1974, are coded by circle sizes. (From Cleveland et al. (ref. 22), copyright 1976 by the American Association for the Advancement of Science; reproduced with permission.)

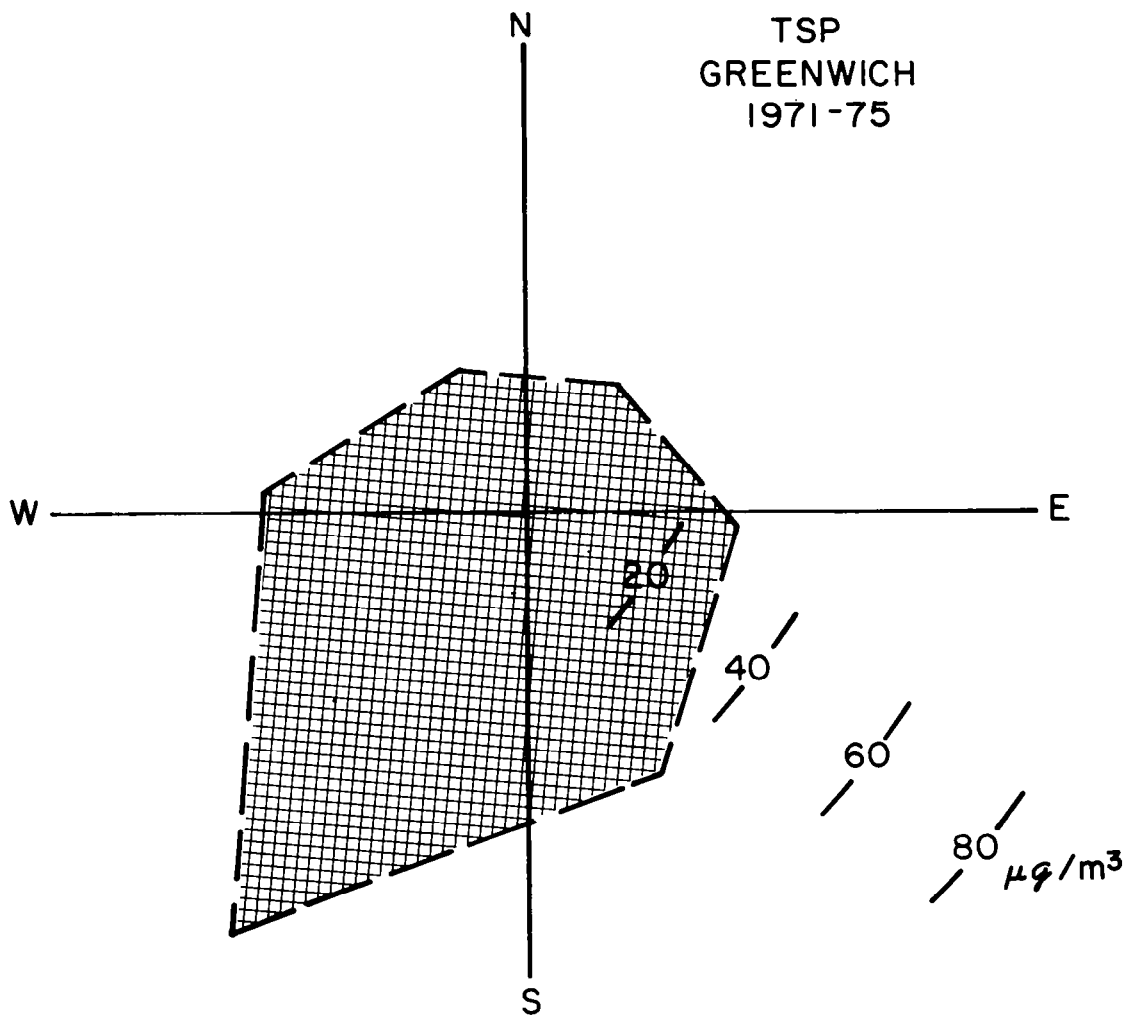


Figure 8.- Total particulate matter as a function of wind direction in Greenwich, Conn., from 1971 to 1975. New York-New Jersey metropolitan area is southwest of this monitoring site (Bruckman (ref. 23)).

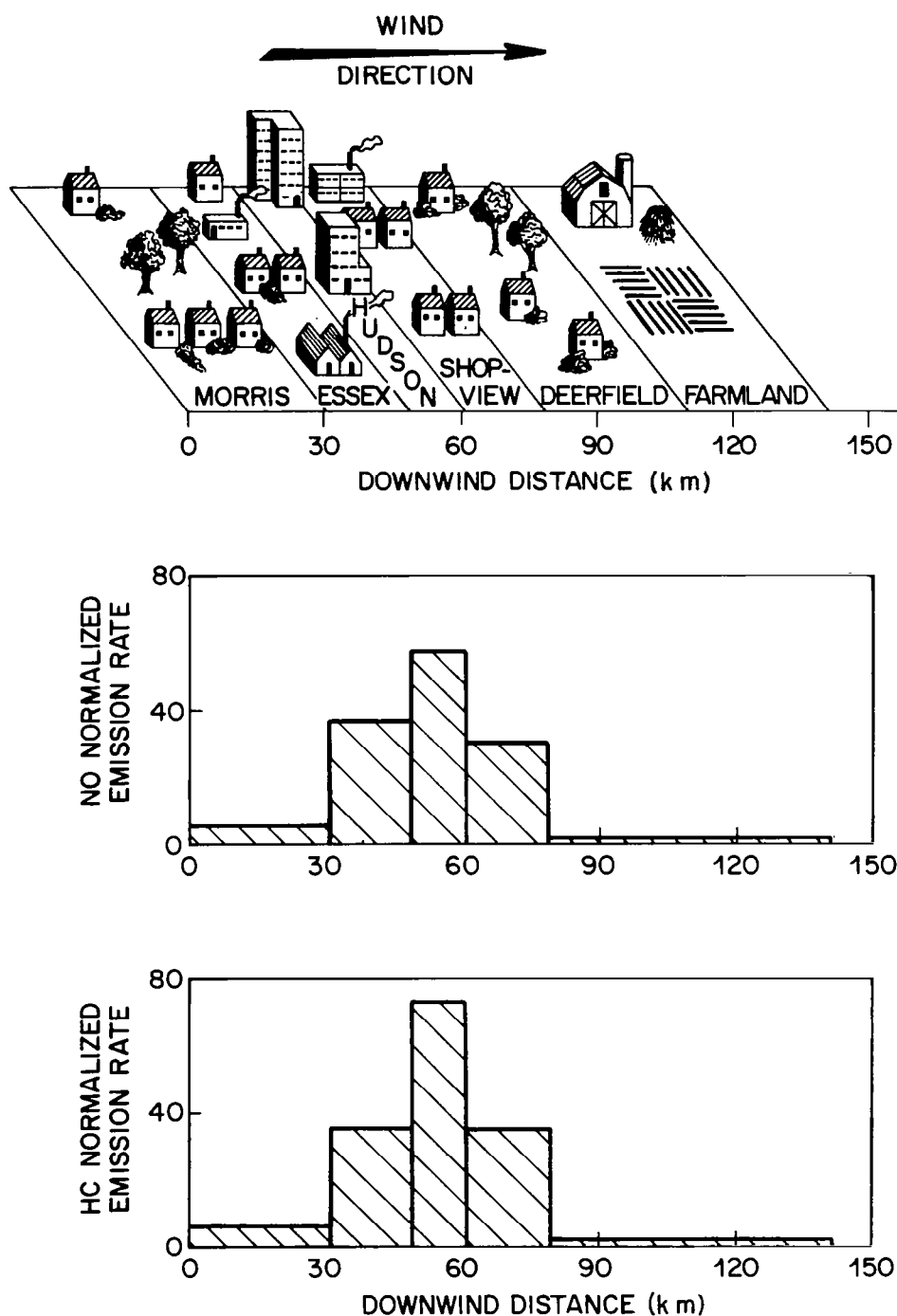


Figure 9.- Six-county computational sequence showing respective downwind distances (referenced to western edge of Morris County) and relative NO and hydrocarbon (HC) emission rates (for relative rate purposes, Deerfield and Farmland Counties' emission rates have unity values).

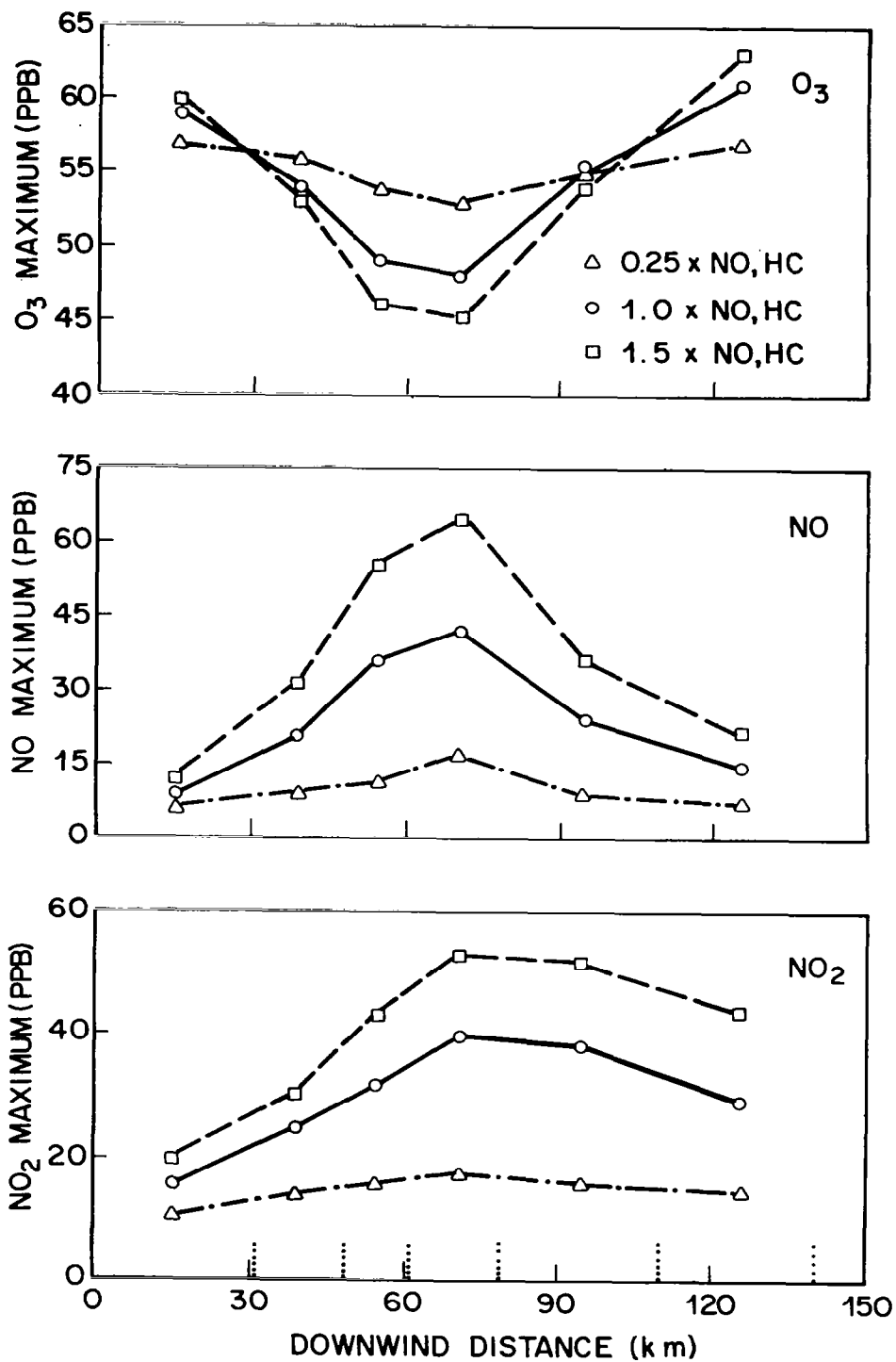


Figure 10.- Computed diurnal maximum concentrations of NO, NO₂, and O₃ in the six counties. Dotted lines on abscissa indicate county boundaries.

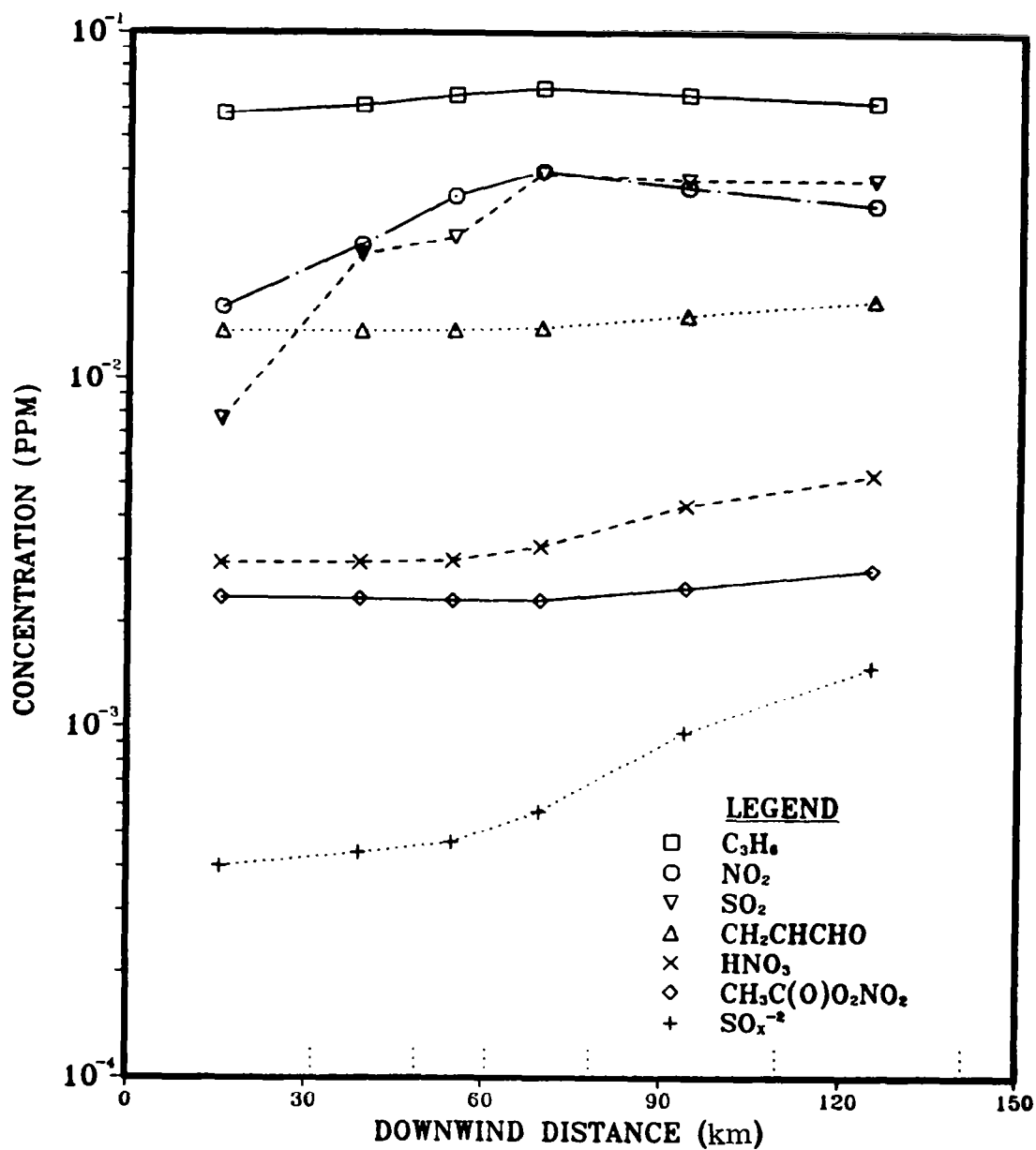


Figure 11.- Computed concentrations of precursors (NO_2 , C_3H_6 , and SO_2) and photochemical products (SO_x^{-2} , HNO_3 , $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$, and CH_2CHCHO) in the six counties at 7 p.m. for days with normal emissions, sun, and wind. Dotted lines on abscissa indicate county boundaries.

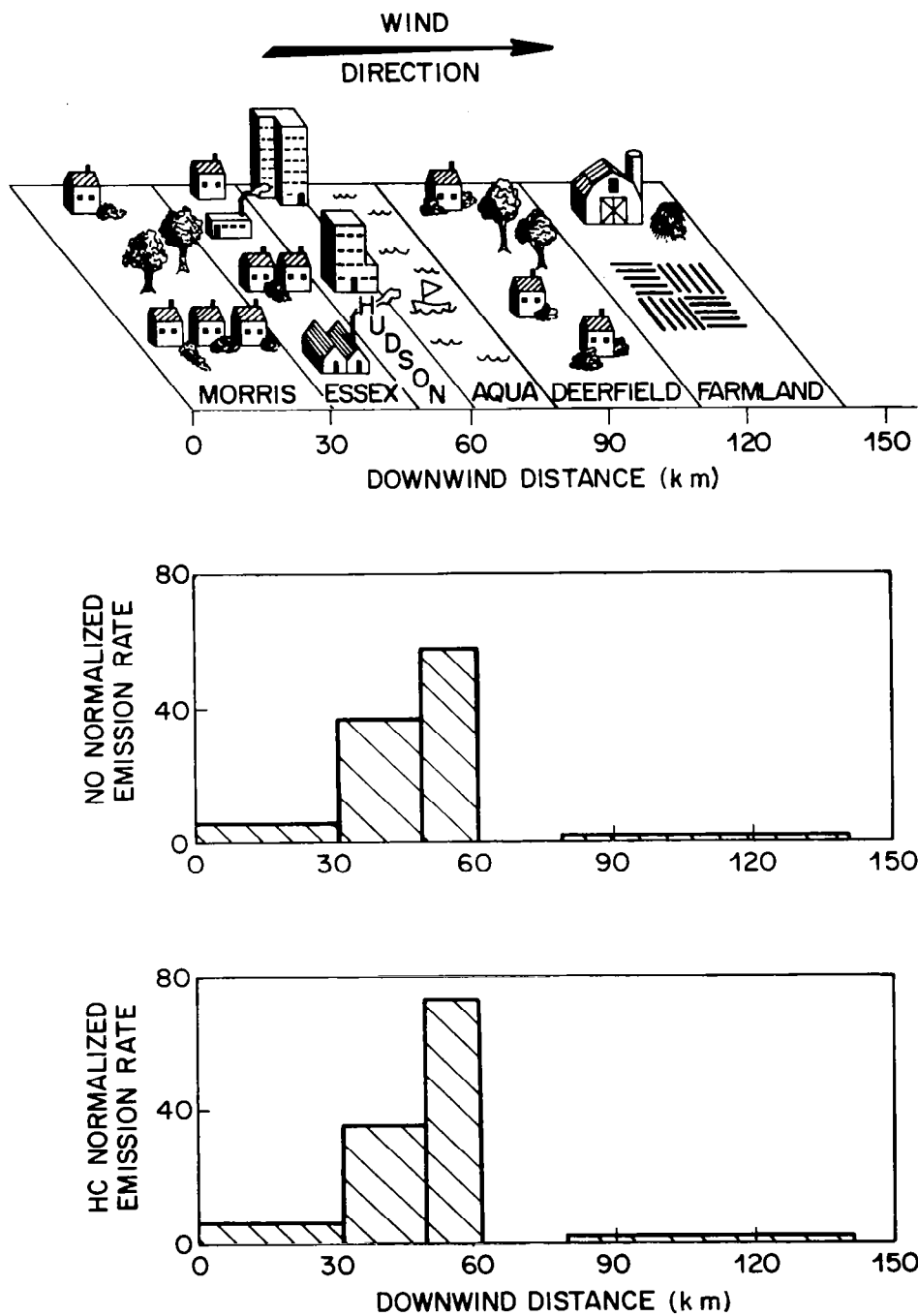


Figure 12.- Six-county computational sequence for overwater traverse together with normalized NO and hydrocarbon (HC) emission rates.

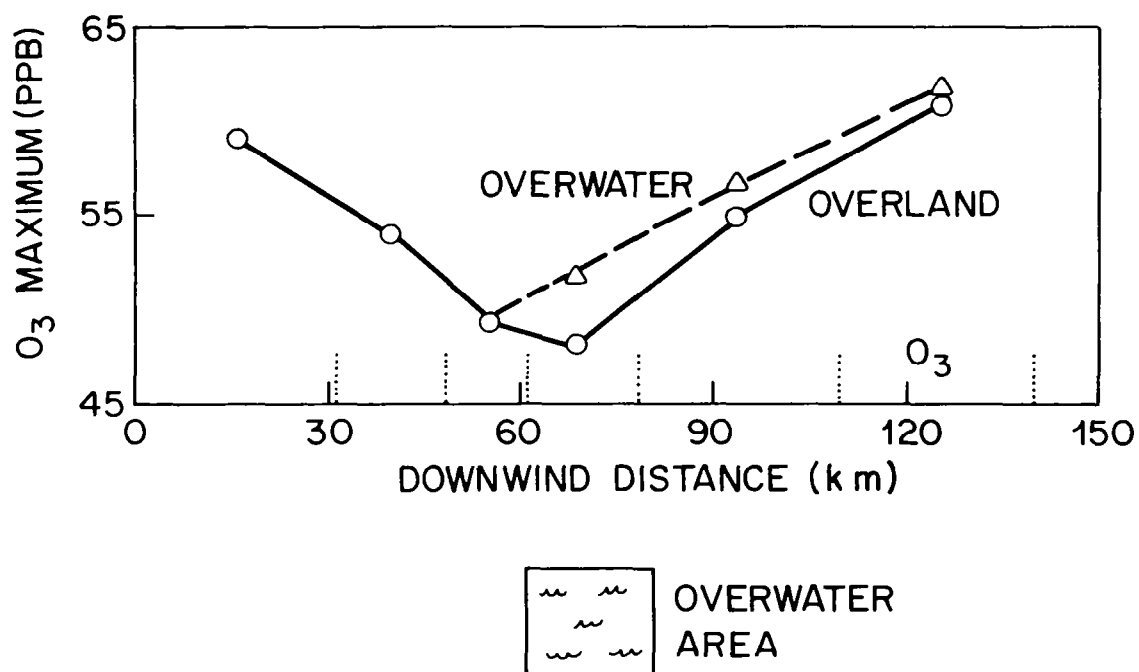


Figure 13.- Maximum computed ozone concentrations for overland and overwater traverses. Plotted points are averages over individual counties. Dotted lines on abscissa indicate county boundaries.

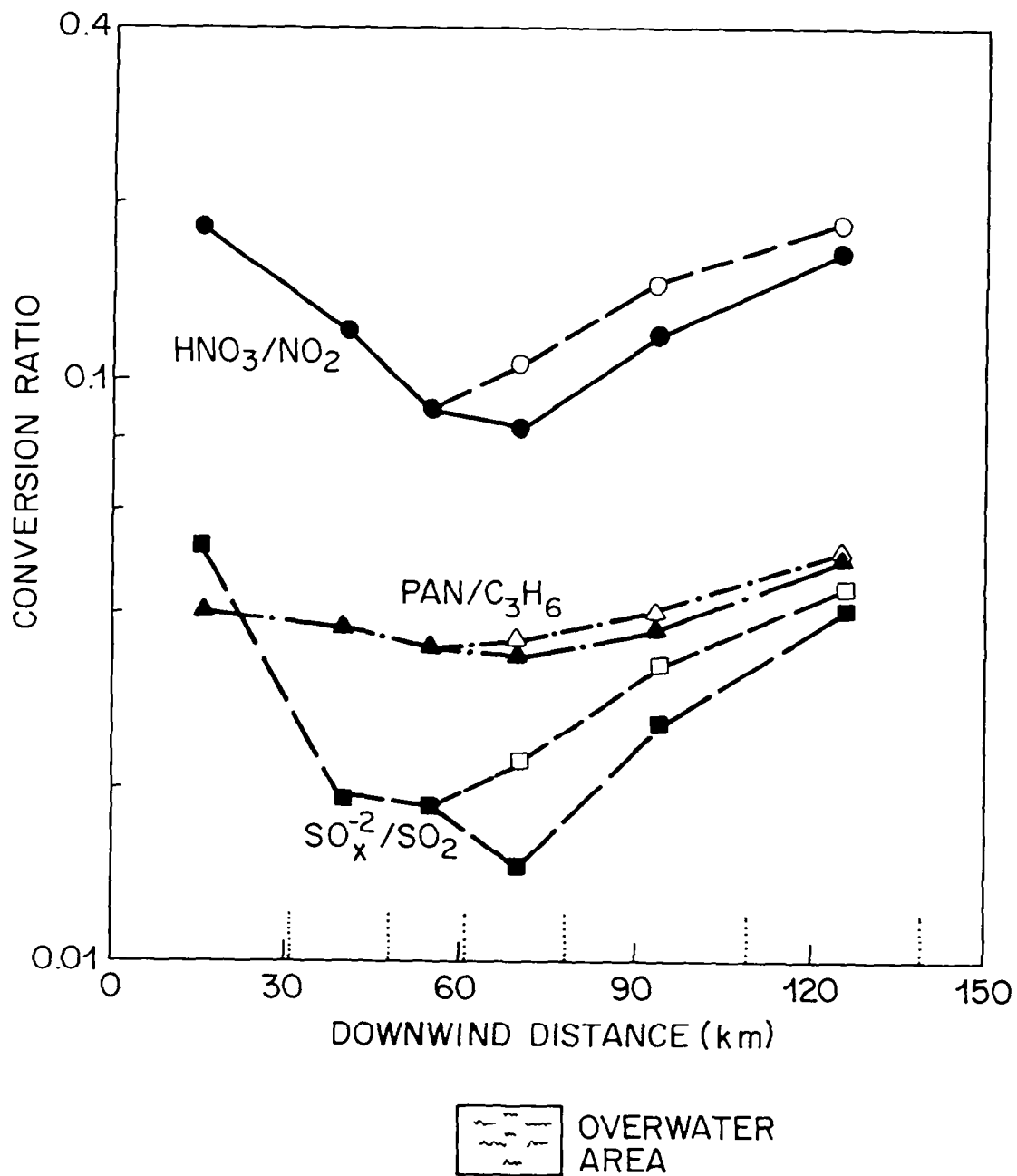
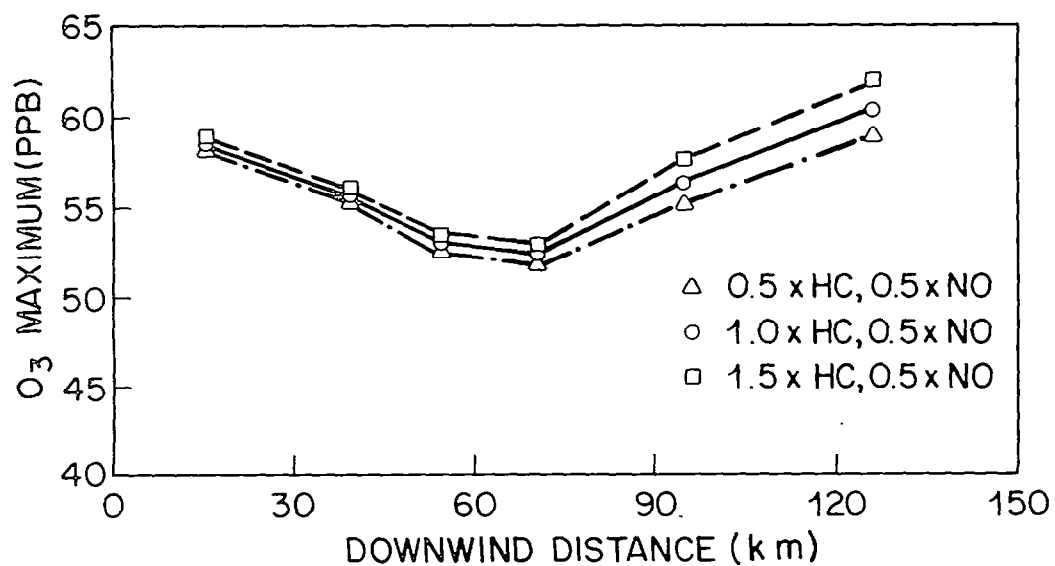
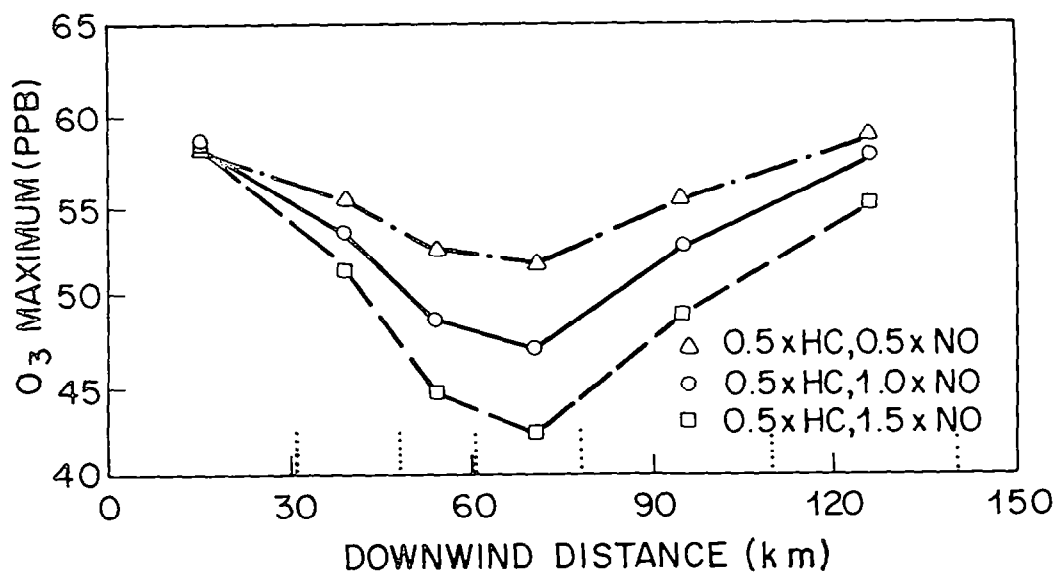


Figure 14.- Conversion ratios for nitrate (circles), sulfate (squares), and PAN (triangles) as functions of downwind distance at 7 p.m. Solid symbols refer to overland traverse and open symbols to overwater traverse. Dotted lines on abscissa indicate county boundaries.



(a) Variation of hydrocarbon emissions only.



(b) Variation of NO emissions only.

Figure 15.- Computed diurnal ozone maxima for the six counties in NO-HC anthropogenic emission plane. Dotted lines on abscissa indicate county boundaries.

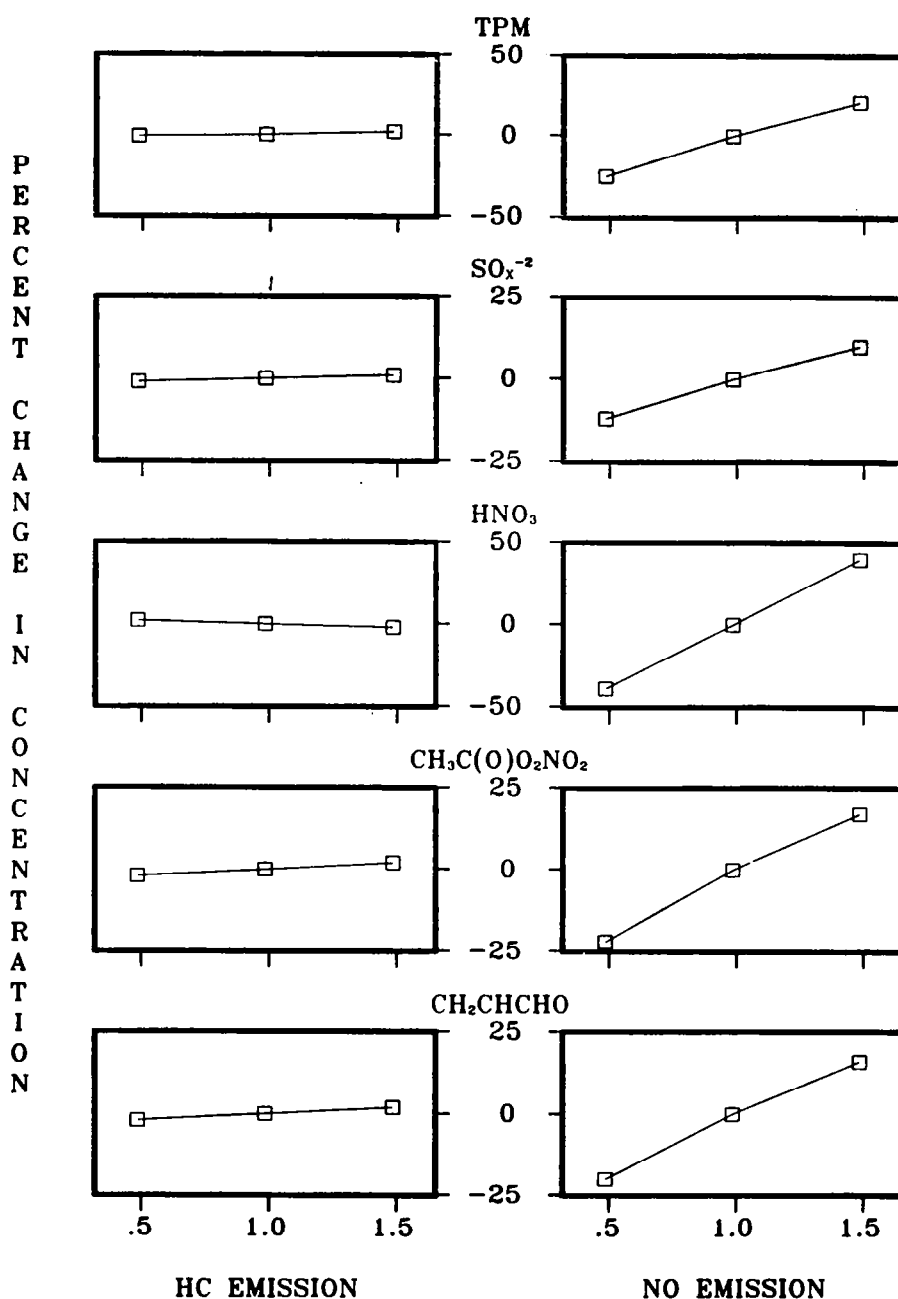


Figure 16.- Percent change in concentration of various photochemical products at 7 p.m. in Hudson County for different emission rates. Plots on the left are for variation in hydrocarbon (HC) emission normalized to current source estimate (Abcissa = 1.0); NO emissions are kept constant at current estimate for these computations. Plots on the right are for variation in NO emission with HC emission kept constant. TPM indicates total particulate matter.

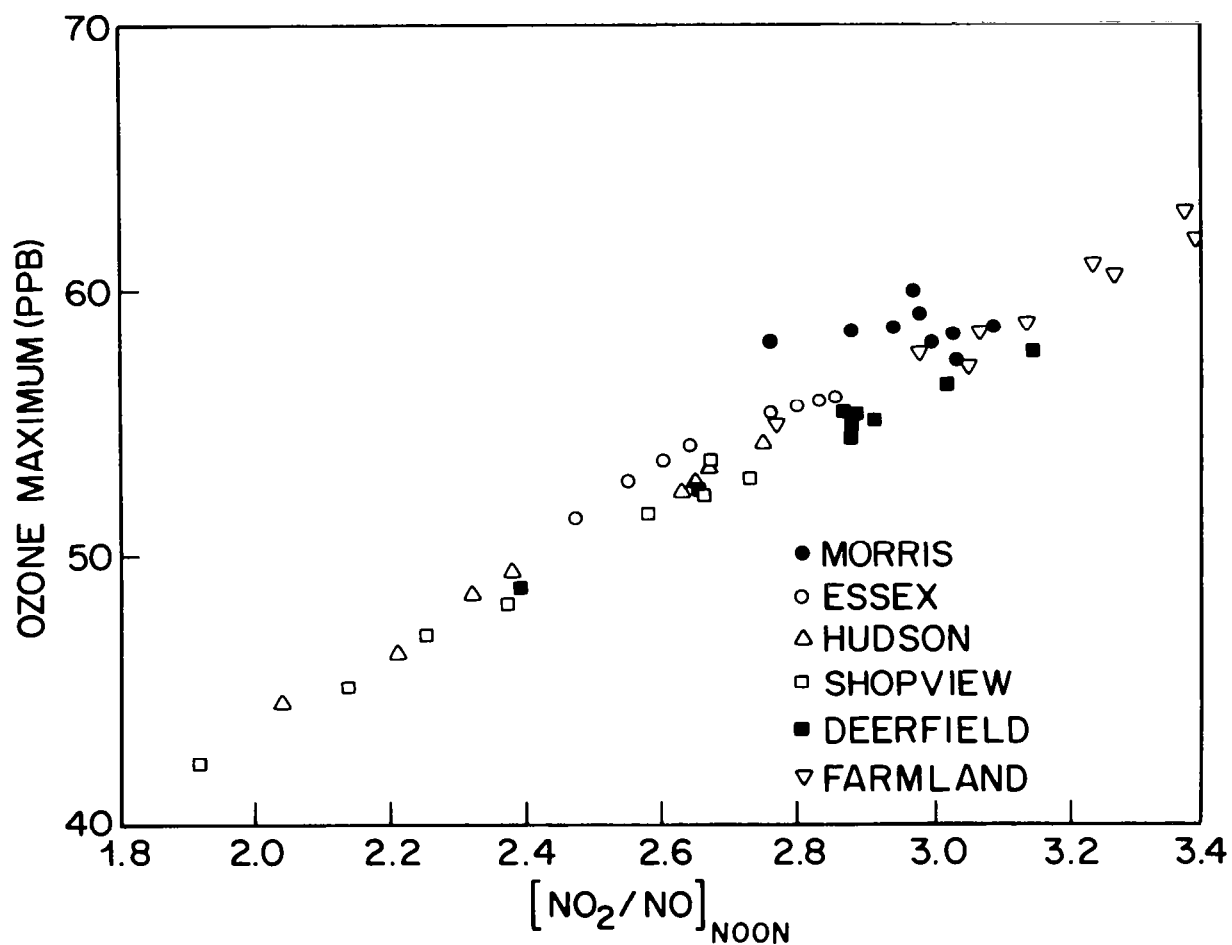


Figure 17.- Computed diurnal ozone maxima in the six counties as a function of noontime NO_2/NO concentration ratio.

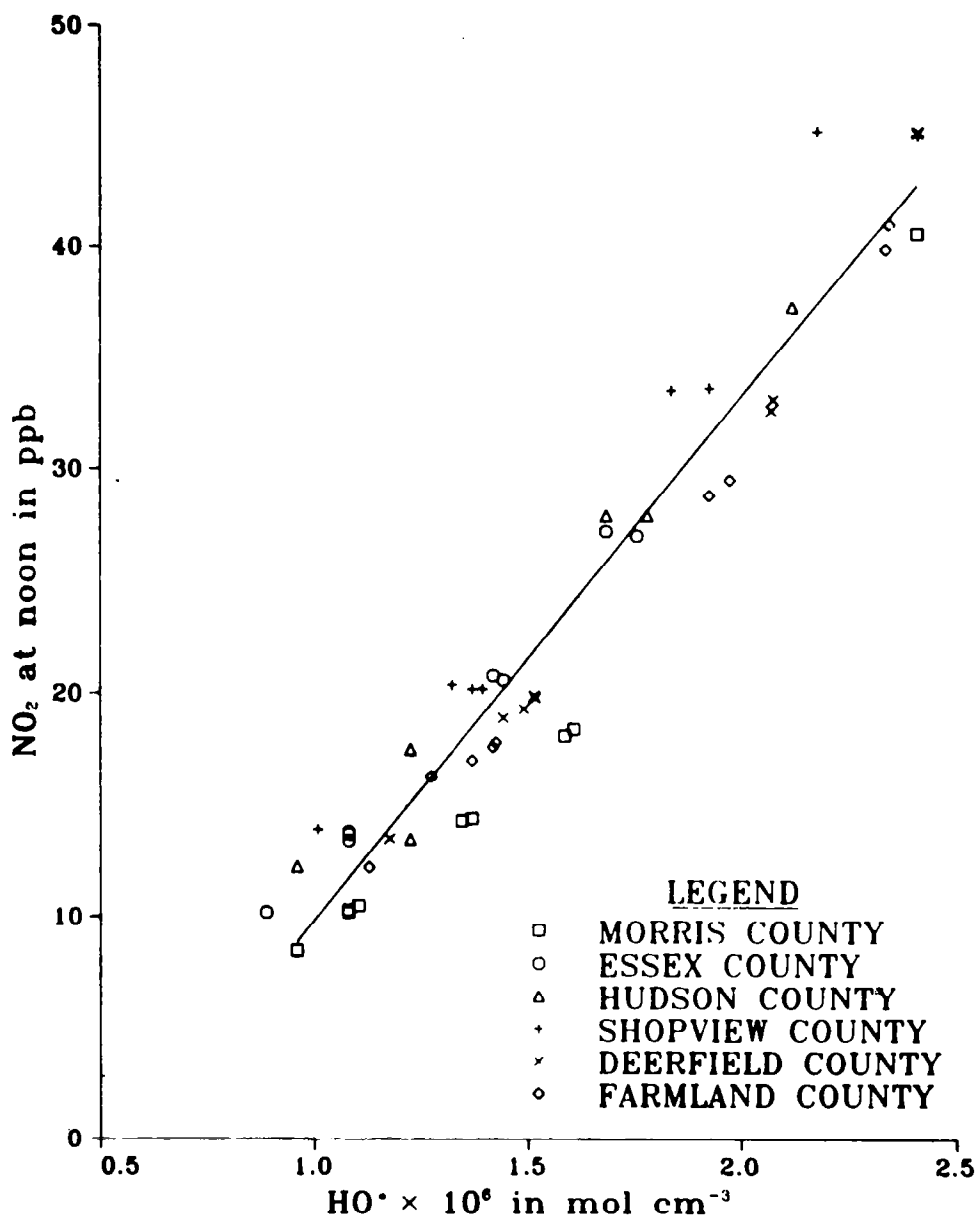


Figure 18.- Relationship between $\text{HO} \cdot$ maxima (molecules- cm^{-3}) and NO_2 noontime concentrations (ppb) for all counties and emission fluxes included in this series of computations.